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Chemistry: Experiments and Principles

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37 **Rb** *85.5*	38 **Sr** *87.6*	39 **Y** *88.9*	40 **Zr** *91.2*	41 **Nb** *92.9*	42 **Mo** *95.9*	43 **Tc** *(99)*	44 **Ru** *101.1*	45 **Rh** *102.9*	46 **Pd** *106.4*	47 **Ag** *107.9*	48 **Cd** *112.4*	49 **In** *114.8*	50 **Sn** *118.7*	51 **Sb** *121.8*	52 **Te** *127.6*	53 **I** *126.9*	54 **Xe** *131.3*
55 **Cs** *132.9*	56 **Ba** *137.3*	57-71 **La-Lu**	72 **Hf** *178.5*	73 **Ta** *180.9*	74 **W** *183.9*	75 **Re** *186.2*	76 **Os** *190.2*	77 **Ir** *192.2*	78 **Pt** *195.1*	79 **Au** *197.0*	80 **Hg** *200.6*	81 **Tl** *204.4*	82 **Pb** *207.2*	83 **Bi** *209.0*	84 **Po** *(210)*	85 **At** *(210)*	86 **Rn** *(222)*
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		57 **La** *138.9*	58 **Ce** *140.1*	59 **Pr** *140.9*	60 **Nd** *144.2*	61 **Pm** *(145)*	62 **Sm** *150.4*	63 **Eu** *152.0*	64 **Gd** *157.2*	65 **Tb** *158.9*	66 **Dy** *162.5*	67 **Ho** *164.9*	68 **Er** *167.3*	69 **Tm** *168.9*	70 **Yb** *173.0*	71 **Lu** *175.0*	
		89 **Ac** *(227)*	90 **Th** *232.0*	91 **Pa** *(231)*	92 **U** *238.0*	93 **Np** *(237)*	94 **Pu** *(242)*	95 **Am** *(243)*	96 **Cm** *(248)*	97 **Bk** *(247)*	98 **Cf** *(249)*	99 **Es** *(254)*	100 **Fm** *(253)*	101 **Md** *(256)*	102 **No** *(254)*	103 **Lw** *(257)*	

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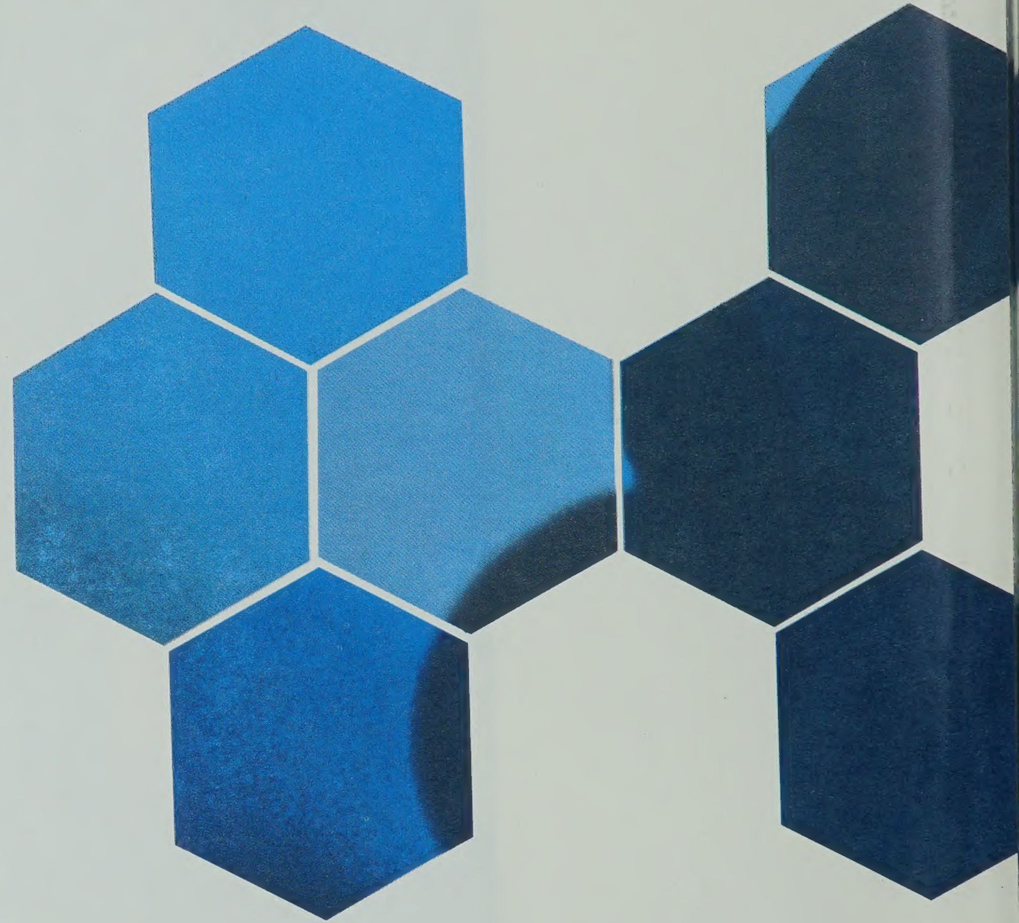
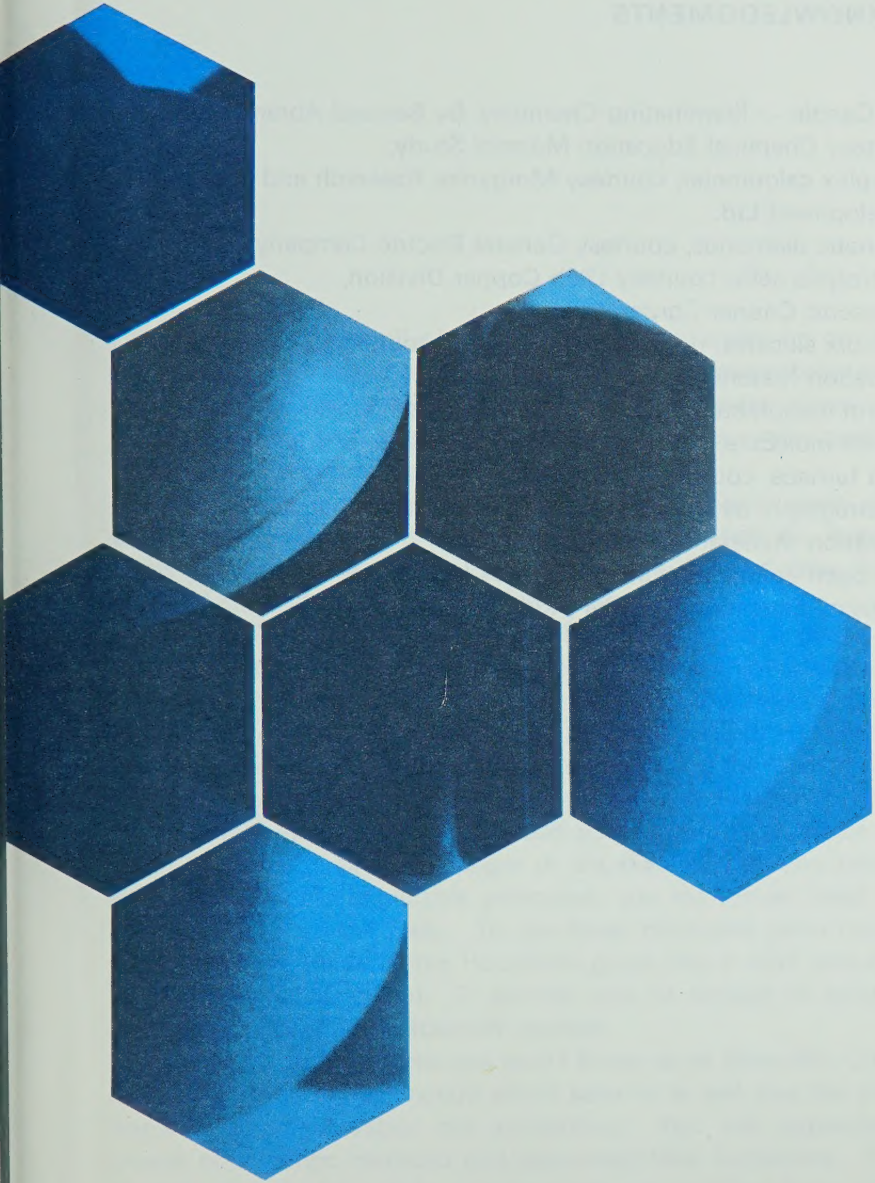
Chemistry: Experiments and Principles





Chemistry: Experiments and Principles

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A Note to the Student

Chemistry deals with all of the substances that make up our environment. It also deals with the changes that take place in these substances — changes that make the difference between a cold and lifeless planet and one that teems with life and growth. Chemistry helps us understand and benefit from nature's wondrous ways.

Chemistry is an important part of science. Since every phase of our daily life is affected by the fruits of scientific activity, everyone should know what scientific activity is, what it can do, and how it works. The study of chemistry will help you learn these things.

CHEMISTRY — EXPERIMENTS AND PRINCIPLES presents chemistry as it is today. It does so with emphasis upon the most enjoyable part of chemistry — experimentation. A clear and valid picture of the steps by which scientists proceed is carefully presented and repeatedly used. Unifying principles are developed, with the laboratory work providing the basis for the development. The experimental theme is supported by a number of films to provide experimental evidence that is needed but not readily available in the classroom because of inherent danger or expense. When you become familiar with these widely applicable principles, you no longer need to memorize innumerable chemical facts. To see these principles grow out of observations you have made in the laboratory gives you a valid picture of how all scientific advances begin. It permits you to engage in scientific activity and to start becoming a scientist yourself.

At the end of this course you won't know all of chemistry. You will know enough chemistry and enough about science to feel that the part you don't know is understandable, not mysterious. You will appreciate the great power of scientific methods and appreciate their limitations. You will have become practiced in making observations, in weighing facts, and in framing valid conclusions. You will have formed the habit of questioning and of seeking understanding rather than being satisfied with blind acceptance. You will be able to share in the excitement of science and feel the pleasure that comes with discovery. When you achieve these things, then you will have had a thorough introduction to science through chemistry. Nothing could be a more important part of your education at a time when science is molding our age.

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Preface

The title, CHEMISTRY — EXPERIMENTS AND PRINCIPLES, emphasizes the theme of this book. A clear and valid picture of the steps by which scientists proceed is carefully presented and repeatedly used. Observations and measurements lead to the development of unifying principles and then these principles are used to interrelate diverse phenomena.

The initial set of experiments and the first seven chapters provide a foundation for this course. The elements of scientific activity are immediately displayed, including the role of uncertainty. The atomic theory, the nature of matter in its various phases, chemical periodicity, and the mole concept are developed early. After presentation of the experimental evidence that led scientists to postulate different models for the atom (Chapters 8 and 9), eight chapters are devoted to the extraction of important chemical principles from relevant laboratory experience. The principles considered include energy, rate and equilibrium characteristics of chemical reactions, acid-base behavior, oxidation-reduction, and chemical bonding in gases, liquids, and solids. The book concludes with four chapters of descriptive chemistry (18–21) in which the applicability and worth of the principles developed earlier are seen again and again.

This book shifts emphasis away from purely descriptive chemistry and toward chemical principles to represent properly the change that has taken place in chemistry over the last decades. Less obvious, but perhaps more important, is the systematic development of the relation between experiment and theory. Chemistry is gradually and logically unfolded, not presented as a collection of facts, dicta, and dogma. We hope to convey an awareness of the significance and capabilities of scientific activities that will help each future citizen assess calmly and wisely the growing impact of technological advances on his social environment. Finally, we have tried to achieve closer continuity of subject matter and pedagogy between high school and modern introductory college and university courses for those students who will continue their science training.

This book follows the pace-setting work of the Chemical Education Material Study. That program, usually called CHEM Study, was one of the curriculum improvement projects supported by the National Science Foundation. This agency of our Federal Government provided support to the creative effort for three years (1960–63) during which time about 30 contributors produced three trial versions and a final set of materials. The contributors were drawn from across the United States and included, about equally, high school teachers and university professors, with industry also represented. All the professors had previously authored textbooks or research treatises. The material was modified by the experience gained in nearly 500 high schools where the trial versions were used. The CHEM Study books and films have been generally available since 1963 and they have earned a place in schools throughout the nation. Test results, just now becoming numerous enough for valid conclusion, suggest that CHEM Study pupils do better in selective college chemistry classes and are not at a disadvantage in regular ones.

This book, with the accompanying Laboratory Manual, and the associated Teacher's Guides are first generation descendants from the CHEM Study project. As one of the authorized revisions of those materials, the present work reflects the talents and dedication of the original CHEM Study team. We are grateful for the opportunity to build on their outstanding effort.

We have made changes. They are based on reactions from our students in high school, university, and teacher institute classes. The principal ones are

—a completely rewritten text; modified to bring fundamental understanding of bonding earlier in the course and to provide somewhat easier reading.

—more descriptive material has been included in the chapters that develop chemical principles.

—a completely reworked laboratory manual in which approximately one-fourth of the experiments are new ones.

—the teacher's guide has been split into two parts: one for the text, one for the laboratory work.

—all problems and exercises have been reconsidered and many new ones added.

These changes are designed to facilitate learning by the beginner; to give him real understanding of the process by which new knowledge is gained; to highlight the distinction between facts, interpretations, and proof; and, of course, to instill some chemical information in an easier way.

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Chemistry: An Experimental Science

1

What is the nature of science?

What is the nature of chemistry?

We shall develop the answers to these questions, not through words alone, but through experience. No one can completely convey through words the excitement of scientific discovery. We shall see the nature of science by engaging in scientific activity. We shall see the nature of chemistry by considering problems which interest chemists.

Our starting point then will be the activities of science. We will *perform* these activities, beginning on familiar ground. On such ground, where *you* know the answer, you will best see the steps by which science advances.

1-1 The Activities of Science

Every form of life interacts with its surroundings in one way or another. Some plants require bright direct sunlight for maximum growth. Other plants grow best in dim light. Direct sunlight stunts their growth. Flower development in many plants depends on the number of daylight hours. Some plants develop flowers during the middle of the summer when there are more than twelve hours of daylight. Other plants flower only in the spring or the fall when there are fewer daylight hours.

Birds and animals maintain constant body temperatures by balancing heat gains and heat losses. Feathers and fur are important in retaining heat energy. When the colder temperatures of winter come, many birds migrate to warmer climates. Some animals grow a heavy coat of hair during the winter. Other animals like the chipmunk hibernate through the winter. The body temperature of the chipmunk drops during his long winter nap. The food requirements for the hibernating animal are much less than during his active period, the warm summer months. It is no coincidence that an animal hibernates during the months when food is most difficult to find.

Man is aware of his surroundings and responds in most complex ways. His eyesight and hearing warn him of dangers. He has learned by experience that certain plants are harmful to him and that some pools of water would poison him. His highly developed brain has led him to control fire and to invent the wheel. Man is more curious than a kitten. His methods of communication far surpass the warning quack of a duck or the mating call of the moose. Man's intellect permits him to respond to his environment in many ways.

He gathers information through observation.
He organizes this information and looks for regularities.
He wonders why the regularities exist.
He communicates his findings to others.

All science is built upon the results of experiments.

These are the basic **activities of science.** Observation is the starting point. Observation is most useful when the conditions which affect the observation are controlled carefully. A condition is controlled when it is fixed, known, and can be varied deliberately. An observation brought under control is called **an experiment.** All science is built upon the results of experiments.

1-2 Observation and Description

Patience and practice are required to become a good observer. Consider an example from your own experience. Think how much can be written about a burning candle! Of course, it takes careful observation, a careful experiment. This means the candle must be observed under controlled conditions. But, how do we know which conditions should be controlled? Be ready for surprises! Sometimes the important conditions are hard to discover. Here are conditions that are important in *some* experiments but are *not* important in the candle experiment.

The experiment is done on the second floor.
The experiment is done in the daytime.
The room lights are on.

Here are conditions that might be important in the candle experiment.

The lab bench is near an open door.
The windows are open.
You are standing close enough to the candle
to breathe on it.

Why are these conditions important? They are important because they may change the result of the experiment. Do they have something in common? Yes, there is the common factor that a candle does not operate well in a draft. Often, important conditions are not as easily recognized as these. A good experimentalist pays attention to the discovery of conditions that must be controlled. His success is often determined by his ability to control them.

Review your own description of a burning candle and compare your essay with the one in Appendix 1. How many of your observations are included there? We see that the burning candle is a fascinating object when subjected to *careful observation* and *detailed description.*

1-3 The Search for Regularities

As the number of observations builds up, one of the first questions that arises is "What regularities appear?" The discovery of regularities permits simplification of the observations. Instead of each observation standing alone, several observations can be classed together and can be used more effectively.

There are pitfalls that exist in the search for regularities. The search is a meandering one, frequently taking wrong turns. In the explanations of the unknown not every step is an advance. Yet there is no other way to proceed except by taking steps. We can see how the search progresses in a fable. A story may help you see how a scientist searches for regularities.

FIGURE 1-1A

Making observations.

Fable: A LOST CHILD KEEPING WARM

Once upon a time a small child became lost. Because the weather was cold, he gathered materials for a fire. He discovered that some of the things he brought back to his campfire burned and others did not. To avoid collecting objects that did not burn, the child made a list.

Things That Burn	*Things That Do Not Burn*
Tree limbs	Rocks
Broom handles	Marbles
Pencils	Paperweights
Chair legs	
Flagpoles	

This list was very helpful to him. Soon, however, flagpoles and tree limbs and broom handles became scarce. The child looked for a regularity in his list to guide him to new objects that would burn. He thought of a generalization, a way to summarize the information on his list.

Cylindrical objects burn.

The next day the child went looking for more material for his fire, but he forgot to bring along his list. However, he remembered his generalization. He brought back to his campfire a tree limb, a cane, and three baseball bats (successful predictions!). What's more, he reflected with pleasure, he had not bothered to carry back an automobile radiator, a piece of chain, and a large door. There was no reason to expect these objects to burn since they were not cylindrical.

The child became confident of his generalization. The next day he used his rule again. He returned to his camp heavily laden with three pieces of pipe, two ginger ale bottles, and the axle from an old car. He did not bother to carry back a large square box full of newspapers.

During the long cold night that followed the child drew these conclusions:

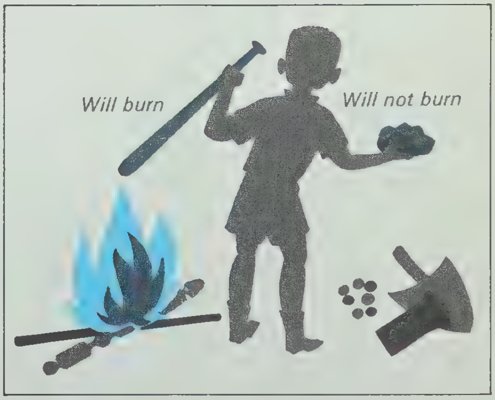

FIGURE 1-1B

Organizing information.

(1) The cylindrical shape of an object may not be related to whether it burns after all.
(2) Even though the "cylindrical" rule is no longer useful, tree limbs, broom handles, pencils, and the other objects in the list do burn.

Thinking about all of the things that he had collected for his fire, the child saw a new regularity.

Wooden objects burn.

What good is this rule in light of the earlier disappointment? Because of the rule the child went back to get the door he had passed up two days earlier. The rule told him not to bring back the chain, the automobile radiator, or the cardboard box full of newspapers.

Don't think this fable is just child's play. It illustrates what science is all about! We make some observations, organize them, and seek regularities to aid us in the use of our knowledge. The regularities are stated as generalizations that lead us to ask "Why?" The answers to "Why?" questions are often analogies. Useful analogies are called **theories.** A theory is used as long as it agrees with the known facts of nature. A theory is used as long as it helps to systematize our knowledge. We can be sure that some day a number of our present scientific views will seem as foolish as the child's "cylindrical objects burn." Don't laugh at the child's slow progress. This child is behaving as a scientist. His faltering steps *will* lead him back to the box of newspapers. The same kind of steps led to the discovery of polio vaccine and to the propulsion of rockets to the moon.

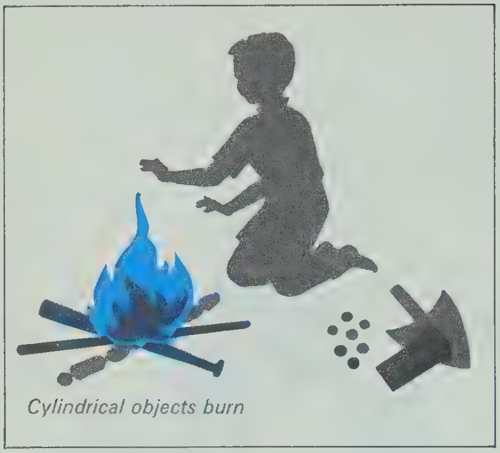

FIGURE 1-1C

Seeking regularities.

1-4 Some Properties of Gases

We will start to learn chemistry by considering some of the substances that might be found in a chemistry laboratory. On the gas cylinders in a chemical stockroom, we find the names ammonia, chlorine, hydrogen, oxygen, hydrogen chloride, nitric oxide, and nitrogen dioxide. Two of these gases can be distinguished by their color. Chlorine is greenish-yellow and nitrogen dioxide is reddish-brown. The other five gases are colorless. The colorless gases can be further sorted according to their solubilities in water. Figure 1-2 shows what happens if a stoppered test tube full of each gas is opened with the mouth of the test tube under water. In the tubes containing ammonia and hydrogen chloride the water rises rapidly, filling the tubes. These two gases dissolve readily in water. In the other three test tubes the liquid levels rise only a little, showing that these gases are not very soluble in water. Ammonia and hydrogen chloride are colorless gases which dissolve readily in water. These two gases can be distinguished by their effect on the moistened dye, litmus. This dye turns red if it is placed in hydrogen chloride. The dye turns blue if it is placed in ammonia.

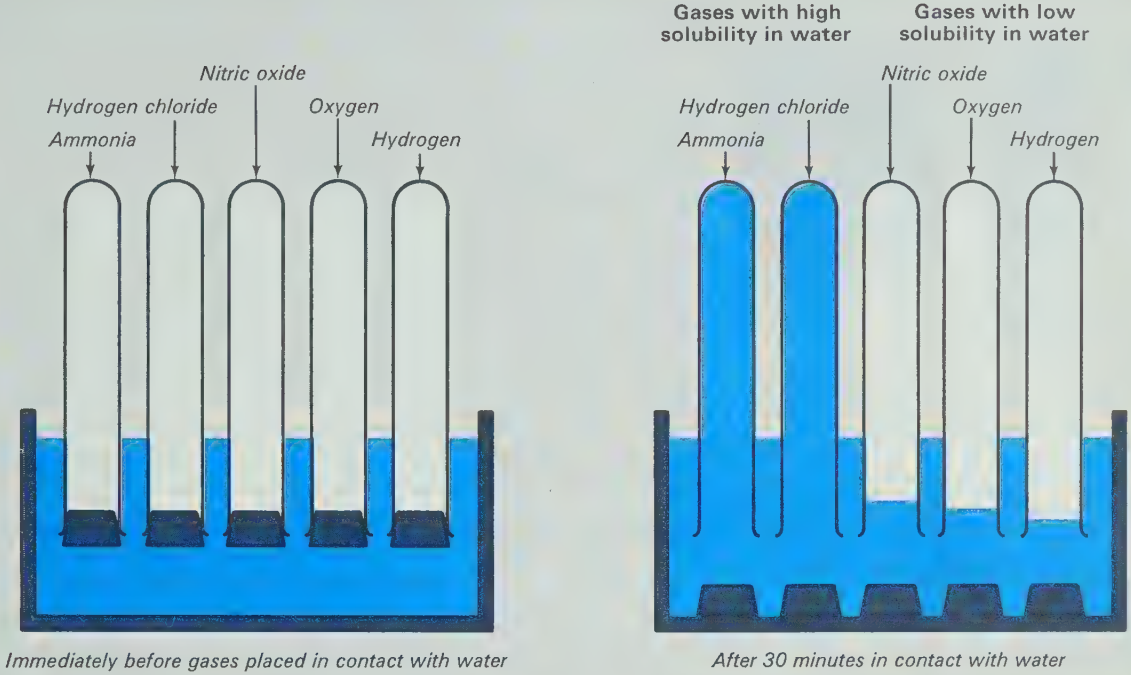
Nitric oxide
Hydrogen chloride
Oxygen
Ammonia
Hydrogen
Immediately before gases placed in contact with water
Gases with high solubility in water
Gases with low solubility in water
Nitric oxide
Hydrogen chloride
Oxygen
Ammonia
Hydrogen
After 30 minutes in contact with water

FIGURE 1-2 Gases have different solubilities in water.

We have not yet distinguished the gases nitric oxide, hydrogen, and oxygen. Nitric oxide has its own personality. Immediately upon exposure to air, this colorless gas becomes reddish-brown, exactly the color of nitrogen dioxide. Neither oxygen nor hydrogen behaves this way.

Oxygen and hydrogen are readily distinguished by their combustion properties. When a glowing splint is plunged into oxygen, the spark bursts into flame. When a glowing splint is plunged into hydrogen, the spark is either extinguished or, if air has mixed with hydrogen, it produces a small explosion.

Like the child in the fable, we can make a list of our observations on the behavior of these seven gases. Looking at Table 1-1 we notice some blank spaces. We did not carry out all of the experiments with each gas. However, it would be easy to tell one of these gases from another by making use of the observations in this table.

While studying gases, we noticed that each gas seemed to fill its container, regardless of shape or size of the container. Any gas we may select has the property of expanding to fill its container. You

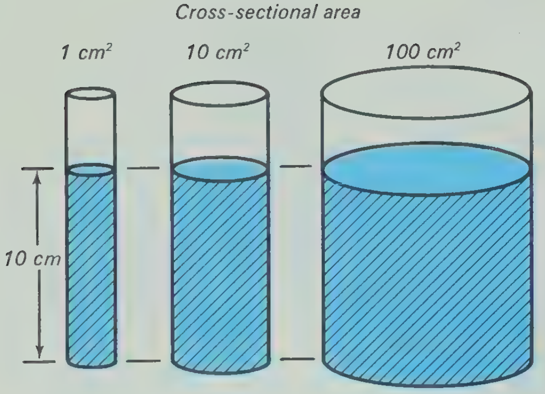

FIGURE 1-3

Three cylinders with different cross-sectional areas.

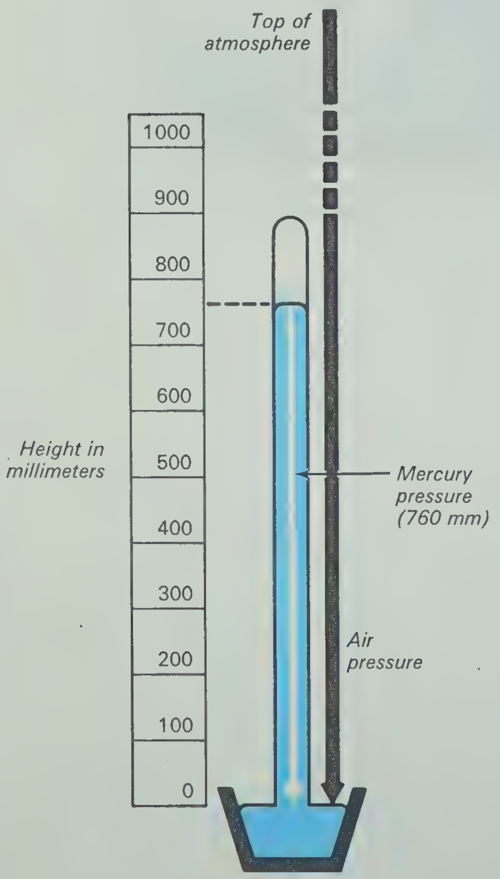

FIGURE 1-4

A barometer measures atmospheric pressure by balancing air pressure against mercury pressure.

TABLE 1-1

Experiments and Observations on The Behavior of Seven Gases

Gas	Color	Solubility in Water	Color Change of Litmus	Glowing Splint Test
Chlorine	greenish-yellow	—	—	—
Nitrogen Dioxide	reddish-brown	—	—	—
Ammonia	colorless	high	red to blue	—
Hydrogen Chloride	colorless	high	blue to red	—
Nitric Oxide	colorless	low	—	(Experiment cannot be carried out. On contact with air, nitric oxide forms a reddish-brown gas.)
Oxygen	colorless	low	—	Spark bursts into flame.
Hydrogen	colorless	low	—	Spark goes out.

know this from your own experience. If there is a gas leak in your kitchen stove, you can soon smell the gas every place in the room. When you enter a bakery, the pleasant aroma of fresh-baked bread seems to be everywhere.

This property, expanding to fill a container, holds true for colored gases and for colorless ones, for those that dissolve readily in water, and for gases that have low solubility. This regularity for gases is in marked contrast with what we find for liquids and solids. A solid object has a definite shape and volume. A liquid has a definite volume but flows to take the shape of its container. Only a gas has the property of expanding to fill any container, regardless of its shape or volume. All gases exhibit this regularity.

An important property of a gas is the pressure it exerts. We have all had many experiences that help us understand what is meant by gas pressure. If we inflate a car tire with air, the pressure in the tire increases. The tire can now support the weight of the car. If we drive up to the top of a mountain, the air pressure on our eardrums changes. A scientist often measures the pressure of a gas by measuring the height of a mercury column supported by the gas.

EXERCISE 1-1

Figure 1-3 shows three cylinders with different cross-sectional areas. Mercury is poured into each of these cylinders until a depth of 10.0 cm is reached. Calculate the pressure in grams/cm^2 at the bottom of each cylinder. The density of mercury is 13.5 grams/cm^3.

1-5 Measurement of Gas Pressure

Two conditions that often are important in chemical experiments are temperature and pressure. Both air temperature and pressure vary from day to day and from place to place. Consequently, chemists usually control and measure these conditions. In addition, it is useful to refer many experimental results to a standard set of temperature and pressure conditions. The temperature 0°C* is easy to obtain with an ice water bath. This temperature is one at which thermometers are calibrated. A temperature that is easy to obtain and easy to measure makes a good standard temperature. By international agreement, *the value of 0°C has been accepted as the* **standard temperature** *for gas volumes.*

Air pressure is measured with an instrument called a **barometer.** One is illustrated in Figure 1-4. A barometer can be made by filling a long closed tube with mercury and inverting the tube in a dish of mercury. The mercury level in the tube drops until the mercury column exerts a downward pressure on the mercury in the dish which is exactly balanced by the downward pressure of an air column which reaches from the mercury surface to the top of the earth's atmosphere. Air pressure then can be expressed in terms of the height of the mercury column. In this illustration the air pressure is 760 millimeters of mercury.

By international agreement, *a standard pressure of* **one atmosphere** (*1 atm*) *is represented by a height of 760 millimeters* (*mm*) *of mercury.* Chemists use both units, **millimeters of mercury** and **atmospheres,** in reporting pressures. At times one unit is more convenient than the other. There are many familiar examples where different units mean the same thing. Sometimes we state the cost of something as fifty cents, but other times we may say half a dollar or "four bits." Athletes compete in the 880-yard or half-mile run.

Chemists have accepted 0°C and one atmosphere pressure as convenient standard conditions. These conditions are called **standard temperature** and **pressure** and the abbreviation **STP** is used.

A device similar to a barometer can be used to measure the pressure of a gas. This device is called a **manometer.** In the closed-end manometer, Figure 1-5, there is a balance between the pressure of the gas in the flask and the downward pressure of the mercury column. The gas pressure in the flask is 105 mm of mercury. Gas pressure is stated in terms of mercury height. In the open-end manometer, Figure 1-6, the external atmospheric pressure balances the sum of two pressures, that of the mercury column plus that of the gas.

$$\begin{aligned}\text{gas pressure} + \text{mercury height} &= \text{atmospheric pressure}\\ \text{gas pressure} &= \text{atmospheric pressure} - \text{mercury height}\\ \text{gas pressure} &= 760\text{ mm} - 655\text{ mm}\\ &= 105\text{ mm of mercury}\end{aligned}$$

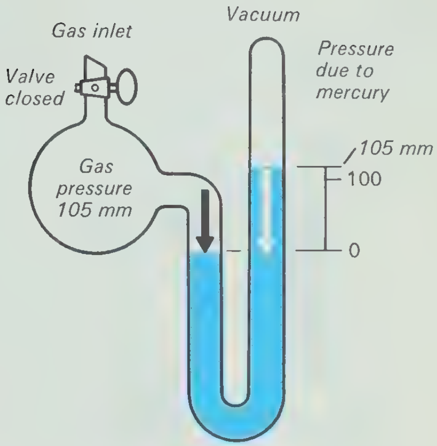

FIGURE 1-5

Closed-end manometer.

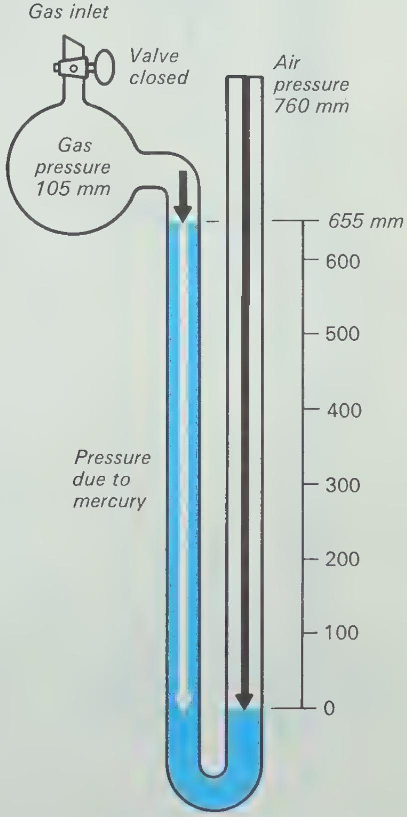

FIGURE 1-6

Open-end manometer.

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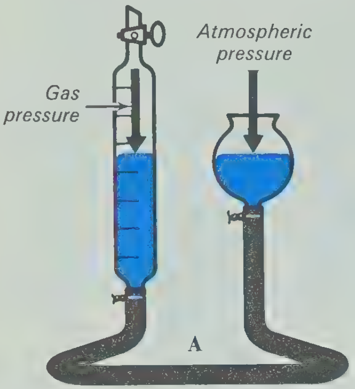
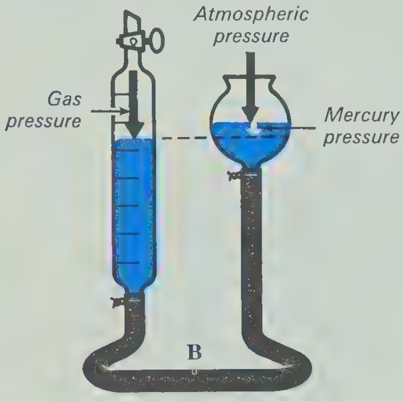
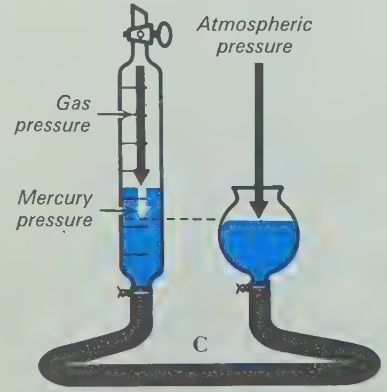
* °C is the symbol for temperature readings made on the Celsius temperature scale. This scale was formerly referred to as the Centigrade scale.



Gas pressure = atmospheric pressure



Gas pressure = atmospheric pressure + pressure due to mercury



Gas pressure + pressure due to mercury = atmospheric pressure

Gas pressure = atmospheric pressure − pressure due to mercury

FIGURE 1-7

Let's look at the experiment illustrated in Figure 1-7. (All our measurements will be made at the same temperature in this experiment.) Some gas is confined in a calibrated measuring tube which is called a **gas buret**. Mercury is in the flexible rubber tube attached to a reservoir or leveling bulb. If we adjust the bulb so that the mercury levels are the same in the gas buret and in the reservoir, the pressure of the gas is equal to the external atmospheric pressure.

As we raise the bulb, the mercury levels change. We can make an observation and suggest an interpretation.

The gas volume decreases.	(Observation)
The gas pressure increases.	(Interpretation)

The gas pressure increases, to balance the mercury height plus the atmospheric pressure. Now if we lower the bulb, the mercury levels change again.

The gas volume increases.	(Observation)
The gas pressure decreases.	(Interpretation)

As long as there is no reaction with mercury, it does not matter what gas is placed in the buret. We always find this regularity in gas behavior, at constant temperature.

> As the pressure on a gas is increased,
> the volume of the gas is decreased.
>
> As the pressure on a gas is decreased,
> the volume of the gas is increased.

1-6 Wondering Why

Undoubtedly many questions have been raised in the discussions of the experiments and demonstrations you have already carried out in this course. Are some of them in this list?

> Why is a candle flame colored?
> Why is heat liberated when a candle burns?
> Why does aluminum metal cause the blue color of the copper solution to disappear?
> Would other metals have the same effect?
> What is the gas that forms when aluminum metal is placed in the copper solution?
> What gases besides chlorine and nitrogen dioxide are colored?
> Why does each metal have its own density?
> Why does a gas expand to fill its container?
> Why does a gas exert pressure?

Perhaps you have never asked yourself questions like these before. A scientist learns to ask questions, and the excitement in science comes in trying to find answers. Often the questions start with the words, "What happens if?" These questions can be answered by doing experiments and making careful observations. Other questions are phrased, "Why does something happen?" These are more difficult questions. In trying to answer questions starting with "Why?", man has been led to ideas that could be developed and tested. The answers often suggest new regularities, new experiments, and new ideas. We search for explanations in trying to answer questions that start with "Why?". Let us see what it means to search for an explanation to the question:

> "Why does the volume of a gas decrease
> when pressure on the gas is increased?"

For a moment we are going to look away from the gas. We can think of a situation that is easy to visualize, one that may provide us with an explanation for gas behavior. Suppose we shake a plastic box containing some steel ball bearings. Of course you know what happens in this case. The ball bearings begin to fly around in a random fashion, colliding with each other and rebounding from the walls of the box. Figure 1-8 illustrates what is happening. We can see and hear these collisions. The ball bearings seem to fill the entire box. If we place our hands on the box, we can feel the ball bearings bounce off the sides. Each time one rebounds from the wall, there is a push or force exerted on the box.

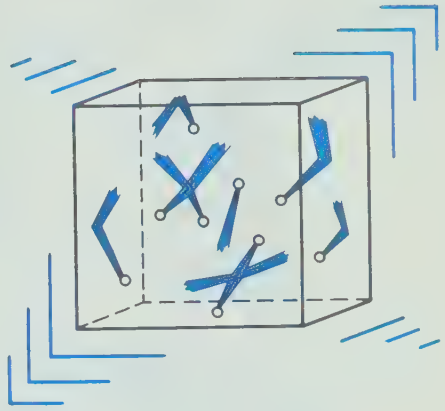


FIGURE 1-8

Ball bearings shaken in a plastic box.

Perhaps a gas is made up of tiny particles too small for us to see, particles that behave like the ball bearings in our example. As the gas particles rebound from the container wall, they push on the wall and exert force. In Figure 1-5 we saw the balance between gas pressure and the pressure of a column of mercury. Our picture of a gas would look like Figure 1-9 now, with gas particles pushing against the mercury surface in the manometer. Doesn't it seem reasonable that the mercury column would be supported if every second a large number of gas particles were pushing against it?

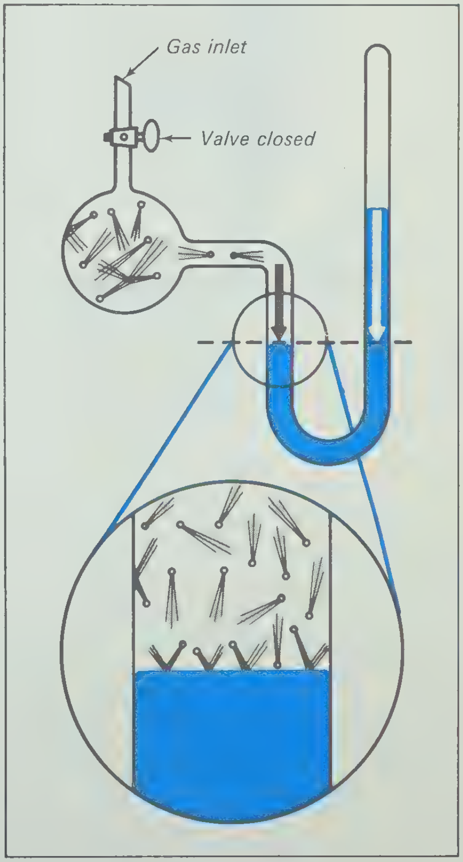


FIGURE 1-9

Gas particles pushing against a mercury surface.

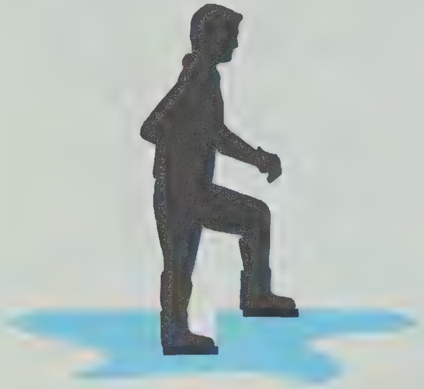
How does our analogy of gas particles and ball bearings agree with some of the observations we have already made?

If we take the stopper from a test tube containing reddish-brown nitrogen dioxide gas, the colored gas rapidly moves out into the room. We notice a sharp, biting odor. If we take the top off the vibrating box containing ball bearings, some of the ball bearings bounce out of the box.

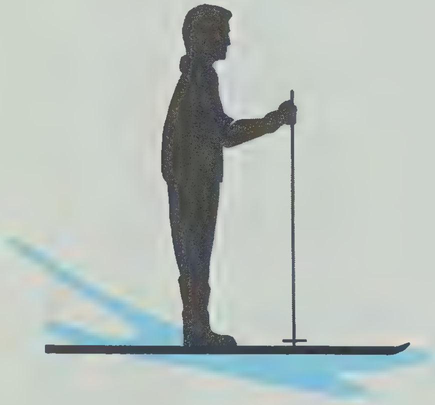
If we increase the volume available to a sample of gas, its pressure decreases. Similarly if we made the box containing ball bearings larger, without changing the number of ball bearings, the number of collisions on the wall every second would decrease. Our analogy seems to be very good.

Starting with a "Why?" question is a common way to search for an explanation about a process that is not well understood. An answer is presented as a description of an analogous system that is well understood. We want to explain a regularity in gas behavior. We try to understand gas behavior in terms of ball bearings in a plastic box. Ball bearings can be seen and studied easily. Although all gases have some properties that are the same, gases also have properties that make them different from each other. If gases are made up of particles, the particles must be different in each gas. It seems reasonable that the particles of one gas, for example ammonia, are not the same as the particles in another gas, hydrogen chloride. The particles that make up a gas determine its properties such as color, odor, and solubility in water. These particles are so important that chemists have given them a special name. The particles making up a gas are called **molecules.**

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$



Man on foot sinks in soft snow



Same man on skis does not sink
The larger area reduces pressure

The molecules of nitric oxide gas cannot be the same as the molecules that make up nitrogen dioxide. There must be differences in these molecules to account for the observation that nitric oxide is a colorless gas and nitrogen dioxide is reddish-brown. Yet, when nitric oxide and air are mixed, a reddish-brown gas appears. This color suggests that a change has occurred.

To explain observations like this, we assume that molecules are built of small particles called **atoms.** Now we can explain the differences between two gases in terms of the atoms present in each molecule of the gas. Nitric oxide and nitrogen dioxide differ in the number or the arrangement of atoms. We will see many times in this course that the properties of a substance depend on the number and kinds of atoms it contains.

1-7 Communicating Scientific Information

We can use our experiment on the pressure and volume of a gas to learn how scientists communicate with each other.

We observed a regularity in gas behavior. As the pressure on the gas increases, the volume decreases. This description or qualitative statement is the simplest way to express a regularity. In some respects a qualitative statement is most useful for the scientist because it is so easy to remember. It serves as a guide in thinking about gases. During this course, you will be furnished with many guides like this one.

We can investigate this regularity further by making careful measurements on gases. Let us use a gas buret like the one shown in Figure 1-5 to make quantitative measurements. We will place 32.0 grams of oxygen gas into the apparatus. The temperature of the gas will be held constant, at $t = 0°C$, throughout our measurements. (In the next chapter you will see why we have chosen 32.0 grams of oxygen. The important point is that we have controlled our system.) By raising and lowering the mercury leveling bulb, we can change the gas volume. At the same time, of course, the gas pressure changes. The numerical values for pressure and volume are listed in Table 1-2. These numbers are also presented in a graph in Figure 1-10. The values for pressure are plotted on the y-axis and the values for volume are plotted on the x-axis.

Here are two quantitative ways that scientists use to communicate a regularity. The first is the listing of the experimental data in a table. The second is the visual presentation of the data in a graph. There is still another way that scientists communicate. The mathematical statement of a regularity is sometimes the most useful way to pass

TABLE 1-2

The Pressure and Volume
of 32.0 grams of Oxygen at $t = 0°C$

Pressure (atmospheres)	Volume (liters)	Pressure × Volume (liter atmospheres)
1.00	22.4	22.4
0.90	24.7	22.2
0.90	24.6	22.1
0.77	29.9	23.0
0.75	29.9	22.4
0.50	44.4	22.2
1.10	20.4	22.4
1.25	17.5	21.9
2.00	11.3	22.6
		Average 22.4 ± 0.2

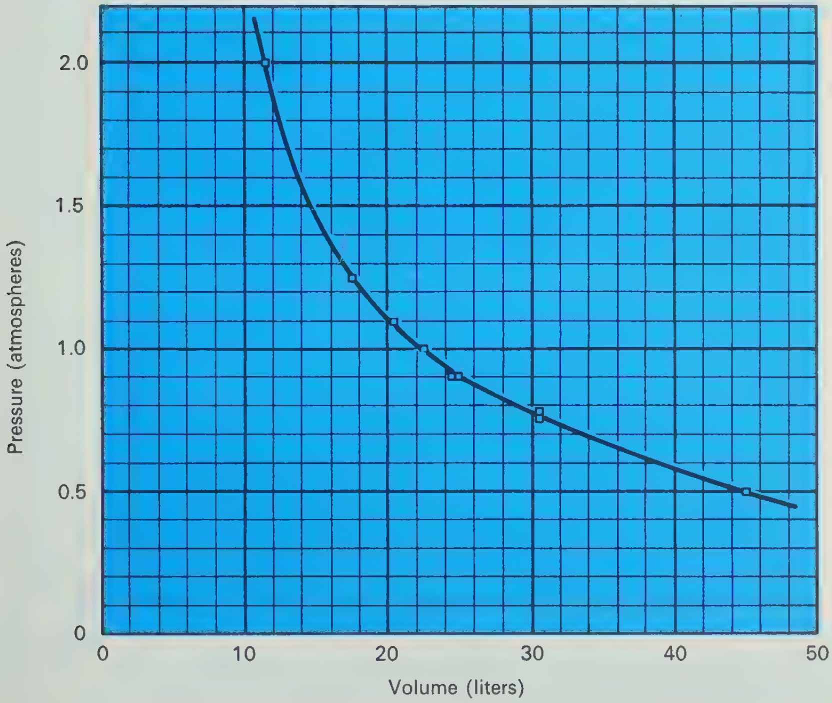
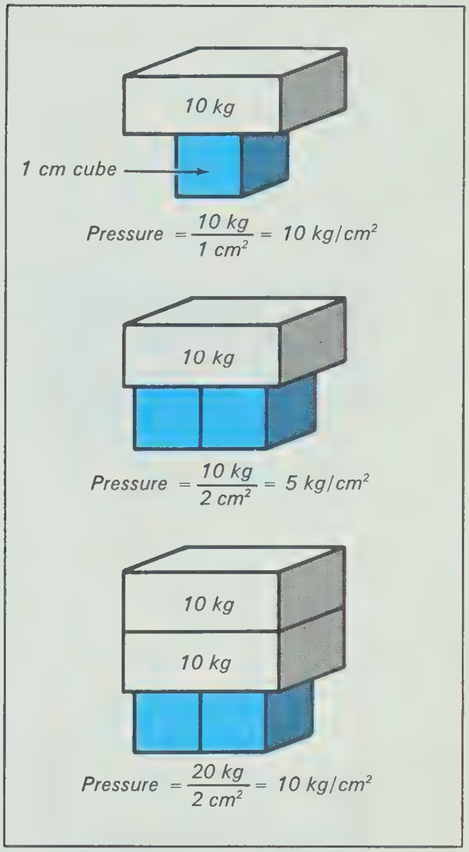


FIGURE 1-10 Pressure *vs* volume data for a gas.

on information. It is the most compact way of stating a regularity. Let us see how to arrive at a mathematical statement of our experimental values.

In the third column of Table 1-2, each value for gas pressure has been multiplied by the corresponding gas volume. We see that this product is approximately the same for all of our measurements. Our qualitative statement of regularity in gas behavior can be expressed quantitatively in mathematical form.


10 kg
1 cm cube
Pressure = 10 kg / 1 cm² = 10 kg/cm²
10 kg
Pressure = 10 kg / 2 cm² = 5 kg/cm²
10 kg
10 kg
Pressure = 20 kg / 2 cm² = 10 kg/cm²

$$P \times V = 22.4 \pm 0.2 \quad (\text{at } t = 0°\text{C})$$
P = pressure in atmospheres
V = volume in liters

This equation can be put back into words. If P increases, V must decrease to give a constant product. If P decreases, V must increase to give a constant product.

There are some variations in the product of pressure times volume. An average of all the values is given in Table 1-2. There is some scatter of the points around the smooth curve in Figure 1-10. This scatter in the data represents the uncertainty that arises in all measurements.

EXERCISE 1-2

a. Add the values of the product PV in Table 1-2 and divide by 9 to obtain the average value.
b. Now, on a separate piece of paper, make a fourth column for Table 1-2 showing the difference between each PV product and the average you have obtained in part a. Head this column with the word "Deviation." Make an entry, for each PV product minus the average value.
c. Add the numbers in the column of deviations (disregarding algebraic signs) and divide by 9 to obtain an average deviation.
d. Compare your calculations in parts a and c with the result in Table 1-2.

1-8 Uncertainty in Science

Perhaps you have already noticed in Table 1-2 that the pressure, 0.90 atmosphere, appears twice. However, the gas volumes for each of these measurements is not the same. This situation is typical of experimental data. Repetition of measurements often gives a series of values that are close to each other. Every measuring device has limitations that fix its precision. Scientists report their experimental values in ways which indicate how carefully they have made their measurements. For the pressure and volume data in Table 1-2, an average is reported for the PV product. The notation ± 0.2 follows the average value, 22.4. What does this notation mean?

Let's look at some examples first before answering these questions. When a scientist sees a number which comes from an experimental measurement, he reacts in a special way. The way in which the number is written is an indication to him of how carefully the measurement was made.

Suppose three people measure a gas volume using different measuring devices. Each makes a report of his measurement.

Report 1. The volume is 22 ± 1 liters.
Report 2. The volume is 22.4 ± 0.2 liters.
Report 3. The volume is 22.414 ± 0.004 liters.

What does a scientist think of these measurements? What does each report tell him?

Report 1. "This measurement was made in a rather approximate fashion. The true volume lies closer to 22 liters than it does to either 21 liters or 23 liters. Although this is not a very precise measurement, it may be good enough for many uses. I could use some simple equipment like that in Figure 1-11A to duplicate this measurement."

Report 2. "This measurement has been made much more carefully than the one in Report 1. The true value lies between 22.2 liters and 22.6 liters. To duplicate this measurement I would choose an apparatus like that in Figure 1-11B. I have to be able to estimate the volume reading to the nearest tenth of a liter."

Report 3. "This measurement is the result of a very carefully performed experiment. I would have to use equipment like that in Figure 1-11C to make such a precise measurement. In addition, I recognize that other conditions, such as temperature, must be carefully controlled. The person who made this measurement is telling me that the true volume lies between 22.410 and 22.418 liters."

Most of the values that you will obtain in your laboratory work in this course will be like the one in Report 2. Some examples are given in Table 1-3.

TABLE 1-3

Some Measurements with Their Uncertainties

Quantity Measured	Numerical Values and Uncertainty	Equipment Used To Make Measurements
Volume	18.5 ± 0.5 milliliters	25 ml graduated cylinder, marked in 1 ml divisions.
Mass	3.06 ± 0.01 grams	Centigram balance.
Temperature	24.4 ± 0.2°C	Thermometer calibrated in 1° intervals.

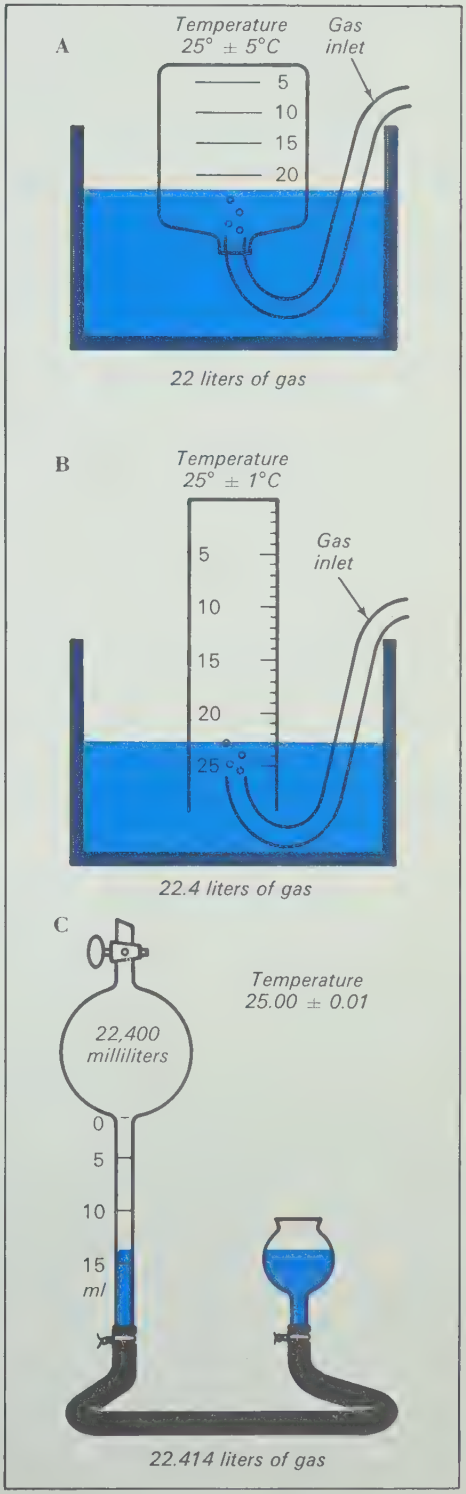


FIGURE 1-11

A. Approximate volume measurement: 22 liters of gas.
B. Fairly careful volume measurement: 22.4 liters of gas.
C. Very careful volume measurement: 22.414 liters of gas.

These ± numbers indicate an uncertainty of approximately 1% for each of these values. Although each of these quantities might be measured with much higher precision, in the laboratory work for this course you should try to make all measurements with an uncertainty of about 1%.

Confidence in experimental values increases with repetition of a measurement. In the laboratory, we shall often pool the results of everyone in the class to achieve repetition.

1-9 Uncertainty in a Derived Quantity

Often scientists want to combine values from experimental measurements to obtain other values which are not measured directly. Such a value is called a **derived quantity.** You have already encountered a combination of measured values in this course. There will be many more examples. In Experiment 3 on density, you divided values for mass by volume to get density, a derived quantity. In the gas behavior demonstration, you multiplied pressure times volume to get a PV product. Since there is uncertainty in any experimental measurement, it is important to know how to estimate uncertainty in derived quantities. We will give you some rules to follow. Remember the uncertainty in a derived quantity is fixed by the uncertainties in the values to be combined. A derived quantity cannot have less uncertainty than that of the separate measurements.

Addition and Subtraction

When metallic aluminum reacts with a copper chloride solution, the temperature of the solution increases. If we want to know the temperature change, we subtract the initial temperature from the final temperature. The change in temperature is called "delta t" and is written Δt. It is the result of two measurements. The change in temperature is a derived quantity.

$$\begin{aligned} \text{Final temperature} &= 88.4 \pm 0.2^\circ\text{C} \\ \text{Initial temperature} &= 26.6 \pm 0.2^\circ\text{C} \\ \Delta t &= 61.8 \pm ?^\circ\text{C} \end{aligned}$$

The uncertainty in reading temperature with a thermometer calibrated in one degree divisions is about ±0.2°C. What uncertainty should we attach to Δt?

Two rules are to be followed in this course in estimating uncertainty of a derived quantity when addition and subtraction are the mathematical operations.

(a) Round off so that all values have the same number of digits after the decimal point.
(b) Add the individual uncertainties to obtain the uncertainty in the derived quantity.

These rules tell us to write: $\Delta t = 61.8 \pm 0.4^\circ\text{C}$

EXERCISE 1-3

Three people give these estimates of the highway distance between towns A, B, C, and D.

A — B	35–40 miles
B — C	45–55 miles
C — D	30–35 miles

Give your estimate of the highway distance from A to C and from A to D. (A to C, 80–95 miles)

EXERCISE 1-4

Three students measure out different volumes of water, using a 25 ml graduated cylinder. After writing his value on the chalkboard, each student transfers his sample to a 100 ml beaker. The three samples are:

$$22.5 \pm 0.5 \text{ ml}$$

$$18.0 \pm 0.5 \text{ ml}$$

$$24.0 \pm 0.5 \text{ ml}$$

What is the total volume of water in the beaker and what is its uncertainty?

Multiplication and Division

The derived quantity PV comes from the combination of two experimental measurements, gas pressure and gas volume. We want to be able to estimate the uncertainty in the PV product.

$$P = 1.25 \pm 0.01 \text{ atmospheres}$$

$$V = 17.5 \pm 0.1 \text{ liters}$$

$$PV = 21.9 \pm \text{ ? liter atmospheres}$$

The ± numbers tell us that each measurement has an uncertainty of about 1% (not 10% and not 0.1%). The product, PV, should then have an uncertainty of about 1%. We will adopt some simplified rules to estimate the uncertainty in a derived quantity obtained by multiplication or division of two measured numbers.

(a) Look for the experimental number with the smallest number of digits. Round off all other numbers to the same number of digits. For example, if you want to combine the values 1.25 and 17.534, round off the second one to 17.5. Both numbers now have the same number of digits, three.

(b) Carry out the multiplication or division. Keep the same number of digits in the derived quantity. In our example we would not write the PV product as 21.875. Instead we would round this off to three digits, 21.9.

(c) The percent uncertainty in the derived quantity should be the same as the percent uncertainty in the least certain number used in the calculation. The numbers for P and V have uncertainties of about one percent. The product, PV, should have the same uncertainty. One percent of 21.9 is approximately 0.2. We write:

$$\begin{aligned} P &= 1.25 \pm 0.01 \text{ atmospheres} \\ V &= 17.5 \pm 0.1 \text{ liters} \\ PV &= 21.9 \pm 0.2 \text{ liter atmospheres} \end{aligned}$$

EXERCISE 1-5

An engineer wished to determine the density of a new alloy of magnesium. He found that a sample weighed 33.35 ± 0.01 g and occupied 18.6 ± 0.2 ml. Calculate the density and show the uncertainty.

1-10 Review

This chapter began with the statement that you would find through experience what science is all about. You have already had opportunities to do so in the laboratory program for this course. Let us review some of the experiments and demonstrations with emphasis on the activities of science.

A. Gathering Information through Observation

Many observations can be made of a burning candle. Undoubtedly some members of your class recorded observations that others did not see. Some may have included interpretations in their list. It takes careful study and attention to detail to observe any system. If you repeated this experiment at home, you were able to make observations that you missed the first time you tried. It takes practice to become a good observer.

A variety of observations can be made when metallic aluminum is placed in a copper chloride solution. Were you a better observer when you performed this experiment? Don't be discouraged if you missed an observation that a classmate recorded. Some of the greatest scientific discoveries have been overlooked for years. And yet when someone finally makes the vital observation, it is difficult to understand how anyone could have missed it for so long.

There are ways to help you become a good observer. One of the most important is to keep a careful record in your notebook of everything you see, at the moment you see it. Try to make your notebook as neat, legible, and complete as possible. Organization makes your notebook more valuable. You will find that planning ahead for an experiment saves you time, time that you can use in making observations. Remember chemistry is built on the results of experiments. And a good experimentalist is a good observer.

B. Organizing Information and Looking for Regularities

There is more to science than making a list of observations. If that is all that we do, we would soon be overwhelmed by the large number of observations to be recorded. We look for some way to organize our information. It is natural to look for patterns or regularities. Perhaps that is why the search is so interesting, and why the scientist gains so much satisfaction from his work. Perhaps you may experience the same sort of pleasure when you carry out the experiments in this course.

In this chapter we described some experiments that could be used to tell one gas from another. Our observations brought out the differences in properties of the gases we studied. There was one property that all of the gases displayed. They expanded to fill any container. Liquids and solids do not behave in this manner. When we carried out a careful experiment with oxygen gas, we found the regularity that a change in gas volume brings about a change in gas pressure.

Regularities provide an efficient way to summarize the results of many experiments. Regularities also point ahead to predict the results of experiments that we have not carried out before.

C. Wondering Why

It is a short step from finding a regularity to asking why the regularity exists. Scientists seek explanations for "wondering why" questions. Often the explanation is presented as an analogy between a system that we understand and the system that we are trying to explain. An explanation is always tentative. It leads us to further experiments to test the explanation. An explanation, in this sense, is often called a **theory.**

An explanation has been suggested for the regularity in pressure-volume behavior of oxygen gas. A gas was compared with a system that we can see and study directly, ball bearings shaken in a plastic box. More experiments with gases will be outlined in the next chapter. Perhaps our explanation or theory will be strengthened by these experiments. Perhaps we shall be in the same predicament as the child in the fable with his "cylindrical objects burn." Then, like the child, we will search for a new explanation.

Wondering why is the most rewarding activity of science. Learn to ask yourself questions beginning with "Why" when you make observations, in and out of the chemistry laboratory.

D. Communicating with Others

The fourth activity of science is, in many ways, the most important one of all. It is only through communicating ideas to others that a strong framework can be provided for a science. Experimental results must be confirmed and explanations must be tested by others. If it were not for this aspect of science, each generation of scientists would have to start from the beginning.

In this chapter we have discussed four ways that scientists communicate. No matter which way is chosen, the objective is always the same: to tell others what experiments you have performed, what the results are, and how carefully you have made the measurements. In this course, you should try to develop skill in scientific communication. A carefully kept notebook is essential. Recognize that errors are part of any scientific measurement and try to communicate how large these errors may be. Test yourself by asking what your report of an experiment means. It takes practice to become a good observer. It takes practice to learn how to communicate. Remember that in this course you are learning what the nature of chemistry is through your own experience.

Questions and Problems for Chapter 1

1

Name some conditions that should be controlled if you wish to determine how many miles different cars will travel per gallon of gasoline.

2

Name some conditions that should be controlled if you want to determine the effectiveness of various detergents.

3

Name some conditions that should be controlled if you want to determine the vitamin C content of various brands of frozen orange juice.

4

Make a list of the regularities and the differences that you can observe among the various cars you know.

5

Make a list of the regularities and differences that you can observe among the various soft drinks you know.

6

Make a list of the regularities and differences that you can observe among the different classrooms in your school.

7

Name some substances, not mentioned in this chapter, which are gases at room temperature.

8

Hydrogen, helium, and carbon dioxide are gases at room temperature. What differences among the properties of these gases account for the following?

(a) Hydrogen and helium are used in balloons but carbon dioxide is not.
(b) Helium is less dangerous to use.

9

A rock has a mass of 42.0 grams when it is weighed in air. When it is weighed in liquid carbon tetrachloride, the mass of the rock is 34.0 grams. Carbon tetrachloride has a density of 1.59 g/ml.

(a) What is the volume of the rock?
(b) What is the density of the rock?

10

Calculate the density of an irregularly shaped object using these data. Water displacement was used to determine the volume of the object. Express your answer to the correct number of digits. (Use the value 1.00 g/ml for the density of water.)

Volume of water in a graduated cylinder, before the object was immersed.	20.0 ml
Volume of water in a graduated cylinder, after the object was immersed.	32.6 ml
Mass of the object in air.	34.0 g

11

Outline a method for determining the density of an object that floats on water.

12

What do you think will happen to the mercury column in a barometer (Figure 1-4, page 6) if you do these things?

(a) Tip the glass barometer tube away from its vertical position.
(b) Carry the barometer up a high mountain.
(c) Lower the barometer to the bottom of a swimming pool.

13

Gas is slowly added to the empty chamber of a closed-end manometer (see Figure 1-5, page 7). Draw a picture of the manometer mercury levels, showing in millimeters the difference in heights of the two mercury levels:

(a) before any gas has been added to the empty gas chamber.
(b) when the gas pressure in the chamber is 300 mm.
(c) when the gas pressure in the chamber is 760 mm.
(d) when the gas pressure in the chamber is 865 mm.

14

Repeat Problem 13, with an open-end manometer (see Figure 1-6, page 7). Use a value of 760 mm for atmospheric pressure.

15

List three different units that could be used to express the speed of a spaceship.

16

In studying the effect of pressure on the volume of a gas, why is it necessary to keep the temperature constant?

17

Suppose in the example of ball bearings shaken in the plastic box that very small ball bearings were used. Would it be so easy to detect a single collision? Would the pressure on the walls be much greater, much less, or approximately the same for the smaller ball bearings? Justify your answer.

18

Consider a box of ball bearings being shaken at a constant rate. What would happen to the number of collisions between ball bearings and walls if the box were made smaller?

19

The balloons that are used for weather study are quite large. When they are released at the surface of the earth, they contain a relatively small volume of gas compared to the volume they acquire when aloft. Explain.

20

Give several examples of two variables that are related so that when one variable increases, the other decreases. Example, pressure and volume of a gas.

21

Express mathematically the relationship between the number of days you have lived and your age in years. Ignore the number of leap years that may have occurred during your lifetime. How could you modify your mathematical equation to take into account leap years?

22

In 1960 a ten-year Census of the United States was carried out. The population of a large city was stated to be 3,846,523. How do you react to that figure? How would you have reacted before you began to study this book?

23

Which do you think would cost more, a cube of iron 1 inch on each edge or a cube of iron 1.000 inch on each edge? Why?

The Atomic Theory

2

One of the activities of science is the search for regularities. Regularities are patterns or generalizations that we can identify in experimental observations. The word **law** is sometimes applied to the older scientific generalizations. For example, the gas behavior described by the equation $PV =$ a constant, is called Boyle's Law. Robert Boyle discovered this regularity in 1660. Modern scientists do not like to use the word law in talking of new regularities or generalizations. It is easy to see why. Most people think of a law as something that is permanent, with penalties if the "law is broken." Certainly it would be very inconvenient if the federal or state laws by which our society operates were to change every week or so.

Scientists continually are testing their generalizations, by making more precise measurements and by devising new experiments. New techniques and new instrumental methods are developed each year. The observations that a scientist can make frequently show that his original generalizations apply only over a limited range of experimental conditions. Somehow changing a "generalization" seems less drastic than changing a "law." As science progressed, the word law was avoided more and more.

When seeking an explanation, we sometimes test out more than one model or theory. The most useful model or theory is retained. A useful theory often suggests new directions of thought. The new directions guide us to new experiments. Additional experimental facts come to light. Sometimes the new facts require growth of the theory. Occasionally these facts contradict the theory. The theory must be abandoned in favor of another. Both the growth and replacement of theories reflect increase in our understanding of the environment.

Let us see how a theory grows.

2-1 Implications and Growth of a Scientific Theory

We can explore our explanation that gas behavior results from randomly moving molecules. We ask a question. Why does gas pressure increase when the gas volume is decreased?

The answer is a possible model for a gas. Perhaps it contains many molecules that are in constant motion. This system can be compared to ball bearings shaken in a plastic box. As the molecules rebound from the walls of their container, they push on the walls. Since there are many molecules striking the wall each second, we must add together all the individual pushes. This is what is meant by gas pressure. What if the container is half as big without changing the number of molecules? Now there are twice as many molecules per unit volume. With twice as many molecules per unit volume, the frequency of wall collisions will be doubled. Doubling the wall collisions will double the pressure. Our model is consistent with the equation:

$$PV = (2P)(\tfrac{1}{2}V) = \text{a constant}$$

For 32.0 grams of oxygen gas at $t = 0°\text{C}$, we found experimentally that

$$PV = 22.4 \pm 0.2 \text{ liter atmospheres}$$

Two other common gases are ammonia and hydrogen chloride. Does our theory apply to them as well as to oxygen? We must perform experiments to find out. We duplicate the conditions used in the study of oxygen. Table 2-1 shows pressure-volume measurements for 32.0 grams of gaseous ammonia at 0°C. Table 2-2 shows the same type of data for 32.0 grams of gaseous hydrogen chloride at the same temperature.

Every day during 1966
United States industry made
65,000,000 pounds of ammonia
8,000,000 pounds of hydrogen chloride

TABLE 2-1

Pressure and Volume of 32.0 Grams of Ammonia Gas at $t = 0°\text{C}$

Pressure (atmospheres)	Volume (liters)	Pressure × Volume (liter atmospheres)
0.100	421	42.1
0.500	84.2	42.1
1.00	42.1	42.1

TABLE 2-2

Pressure and Volume of 32.0 Grams of Hydrogen Chloride Gas at $t = 0°\text{C}$

Pressure (atmospheres)	Volume (liters)	Pressure × Volume (liter atmospheres)
0.100	196	19.6
0.500	39.2	19.6
1.00	19.6	19.6

We see that for these two gases PV = a constant at 0°C. Our theory should be useful for these gases as well as for oxygen. However, the numerical value of the constant varies from one gas to another, if the same mass of gas is considered. We have seen that 32.0 grams of oxygen at 0°C and one atmosphere pressure occupy 22.4 liters. The same mass of ammonia at this temperature and pressure occupies 42.1 liters. The same mass of hydrogen chloride occupies only 19.6 liters. How can our theory be modified to account for these differences?

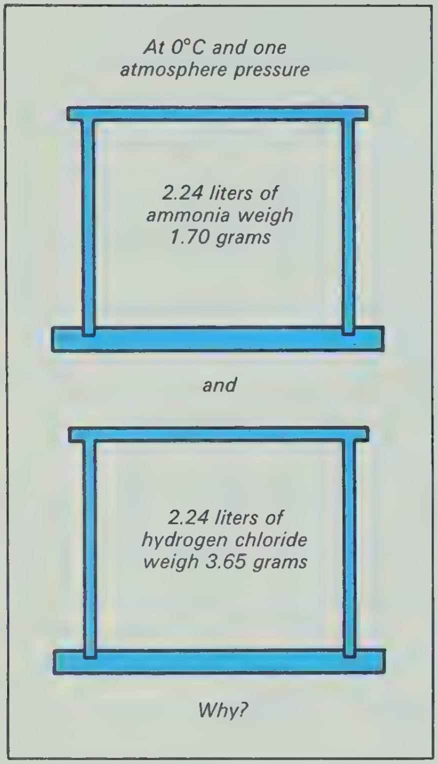

At 0°C and one atmosphere pressure
2.24 liters of ammonia weigh 1.70 grams
and
2.24 liters of hydrogen chloride weigh 3.65 grams
Why?

FIGURE 2-1

SEARCH FOR AN EXPLANATION: Why do equal volumes of ammonia and hydrogen chloride have different masses?

To explain this behavior, chemists have found it convenient to consider a different mass for each gas. They select the amount of gas that gives the same *PV* product as 32.0 grams of oxygen gas. Consider, first, ammonia gas. At 0°C and a pressure of one atmosphere, 32.0 grams of ammonia occupy 42.1 liters. We have taken too large a mass of ammonia. The mass of ammonia needed to occupy only 22.4 liters at this pressure is smaller by a factor of 22.4/42.1.

$$\text{mass of ammonia} = 32.0 \text{ g} \times \frac{22.4}{42.1} = 17.0 \text{ g}$$

Pressure-volume data for this mass of ammonia are shown in Table 2-3.

TABLE 2-3

Pressure and Volume of 17.0 grams of Ammonia Gas at $t = 0°\text{C}$

Pressure (atmospheres)	Volume (liters)	Pressure × Volume (liter atmospheres)
0.100	224	22.4
0.500	44.8	22.4
1.00	22.4	22.4

EXERCISE 2-1

If 32.0 grams of hydrogen chloride gas (at 0°C and one atmosphere) occupy 19.6 liters, then a larger mass of hydrogen chloride is needed to occupy the larger volume, 22.4 liters. Show that the mass needed is 36.5 grams.

Now the regularity between pressure and volume of these three gases can be expressed as follows:

For 32.0 grams of oxygen at 0°C,

$$P \times V = 22.4$$

For 17.0 grams of ammonia at 0°C,

$$P \times V = 22.4$$

For 36.5 grams of hydrogen chloride at 0°C,

$$P \times V = 22.4$$

Each of the gases has a behavior consistent with the regularity PV = a constant. However, the molecules of the gas oxygen must differ from the molecules of the gas ammonia. The nature of the ammonia molecules, then, is the key to the properties of ammonia. The molecules that make up a gas determine its chemical properties.

How do the molecules differ? Why is it that 32.0 grams of oxygen give the same *PV* product as 17.0 grams of ammonia and 36.5 grams of hydrogen chloride (all at 0°C)? We wonder, why do 22.4 liters of ammonia weigh 17.0 grams when the same volume of hydrogen chloride weighs 36.5 grams? Do molecules have different masses?

There are two factors to consider. These are the same factors we would be concerned with if we were to ask why a bag full of marbles weighs 17.0 grams whereas the same bag full of ball bearings weighs 36.5 grams. The explanation would be found by comparing the number of marbles in the bag and the mass per marble to the number and individual mass of ball bearings in a similar bag. In our gas problem we make the same kind of comparison. The mass per molecule and number of ammonia molecules in 22.4 liters must be compared to the mass per molecule and number of hydrogen chloride molecules in 22.4 liters. Here are two possibilities:

(A) Perhaps:
  (1) Equal volumes of these two gases contain the same number of molecules, and
  (2) ammonia molecules weigh less, per molecule, than hydrogen chloride molecules by the factor 17.0/36.5.
(B) Perhaps:
  (1) Equal volumes of these two gases contain different numbers of molecules, ammonia containing fewer by the factor 17.0/36.5, and
  (2) ammonia molecules weigh exactly the same as hydrogen chloride molecules.

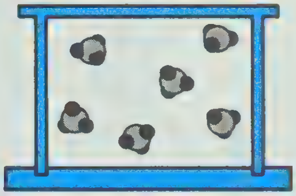
These two possibilities are attractive because they are simple. One factor alone is held responsible in each case. We must be prepared, however, for disappointment. There is the third possibility that neither (A) nor (B) accounts for the properties of gases. We need more information to decide if either proposal (A) or (B) applies to gases. More information is obtained by observing how some gases behave when mixed. As our model grows, we are led again to new experiments.

2-2 Reacting Volumes of Gases

When hydrogen chloride and ammonia gases are mixed, a white powder is formed. When hydrogen chloride molecules and ammonia

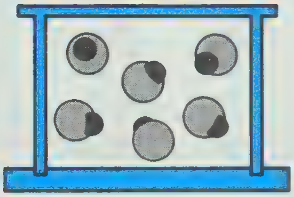
MODEL A

Ammonia



Perhaps: 1. 2.24 liters of ammonia contain the same number of molecules as 2.24 liters of hydrogen chloride.

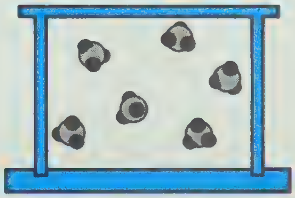
Hydrogen chloride



and 2. Ammonia molecules weigh less than hydrogen chloride molecules (less by a factor, 1.70/3.65).

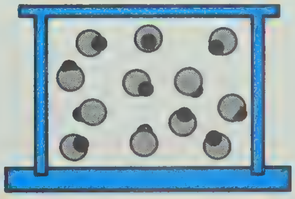
MODEL B

Ammonia



Perhaps 1. 2.24 liters of ammonia contain fewer molecules than do 2.24 liters of hydrogen chloride (less by a factor, 1.70/3.65).

Hydrogen chloride



and 2. Ammonia molecules weigh the same as hydrogen chloride molecules.

FIGURE 2-2

Two simple models to explain the masses of equal volumes of gases.

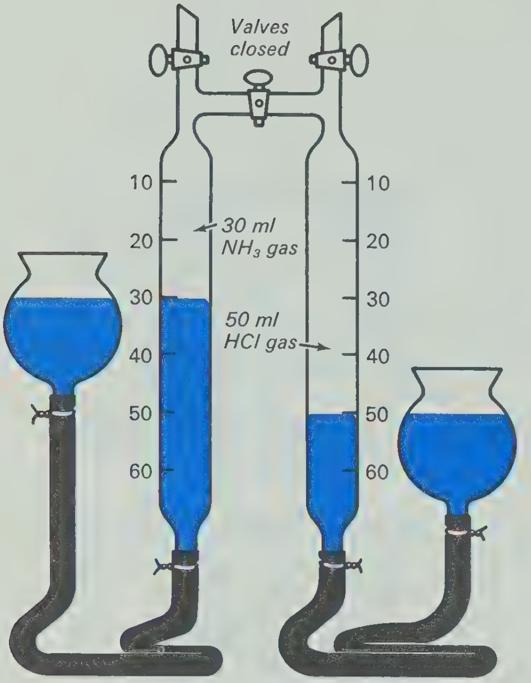


FIGURE 2-3

An apparatus to measure volume changes when gases react.

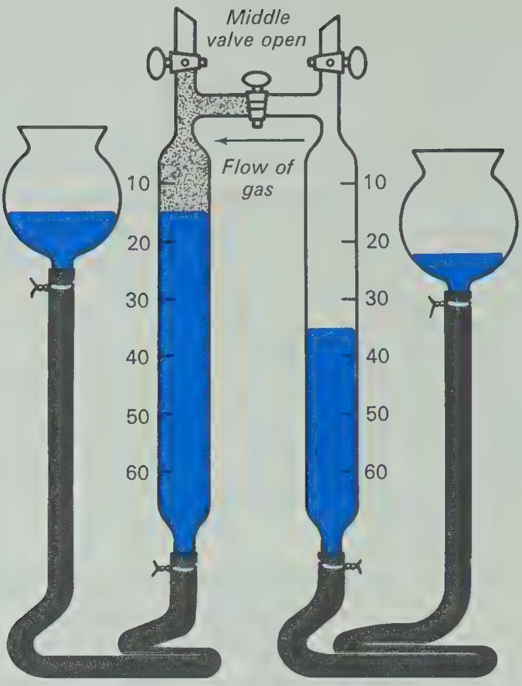


FIGURE 2-4

NH_3 gas reacting with HCl gas.

molecules are mixed, the atoms are rearranged. An entirely different substance, a solid, results. A quantitative study of this process is informative.

Figure 2-3 shows an apparatus suitable for measurement of gas volumes. Thirty milliliters of ammonia have been admitted to the left tube from an ammonia storage tank. Next, fifty milliliters of hydrogen chloride have been admitted to the right tube. The leveling bulbs are used to adjust the pressure of each gas to one atmosphere. The temperature of both gases is, of course, the same. We are ready to carry out the experiment. The hydrogen chloride sample can be transferred slowly into the tube containing the ammonia. Figures 2-4 and 2-5 show the progress of the experiment.

A cloud of the white solid forms in the left tube where the gases mix. Twenty milliliters of hydrogen chloride combine with twenty milliliters of ammonia, forming the white solid. Ten milliliters more hydrogen chloride are just enough to react with the last of the ammonia.

We have an important result. Thirty milliliters of hydrogen chloride combine with just thirty milliliters of ammonia, measured at the same temperature and pressure. Therefore, one liter of hydrogen chloride would combine with one liter of ammonia. Though a given volume of ammonia weighs less than the same volume of hydrogen chloride (less by the factor 17.0/36.5), equal volumes of these gases combine. This simple situation suggests that we should seek a simple explanation. Proposal (A) fits nicely. If we propose that equal gas volumes contain equal numbers of molecules, then thirty milliliters of ammonia and thirty milliliters of hydrogen chloride contain the same number of molecules. Proposal (A) leads us to conclude that one molecule of ammonia combines with one molecule of hydrogen chloride to form the white solid. Through proposal (A), the combining volumes tell us the numbers of molecules that combine. In contrast, there is no correspondingly simple way to explain the new data with proposal (B).

Proposal (A) works very well for the two gases, ammonia and hydrogen chloride. Will it work with other gases? More experiments show that many gases behave as simply as a mixture of hydrogen chloride and ammonia. For example,

1 liter hydrogen + 1 liter chlorine → 2 liters hydrogen chloride

1 liter oxygen + carbon (in coal) → 1 liter carbon dioxide

2 liters hydrogen + 1 liter oxygen → 2 liters gaseous water

These integer volume ratios confirm the usefulness of proposal (A): equal volumes of gases contain equal numbers of molecules. This proposal was first made in 1811 by an Italian scientist, Amadeo Avogadro. It is called **Avogadro's Hypothesis.** It has been used successfully in explaining the properties of gases for more than a century and a half.

> *Avogadro's Hypothesis: Equal volumes of gases, measured at the same temperature and pressure, contain equal numbers of molecules.*

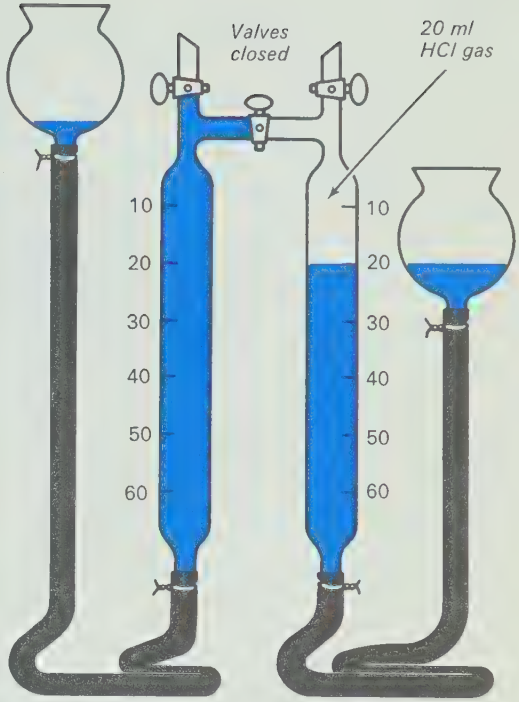


FIGURE 2-5

Completion of reaction between NH_3 gas and HCl gas. 30 ml of NH_3 has reacted with 30 ml of HCl.

2-3 Relative Masses of Molecules

Avogadro's Hypothesis is important because it furnishes a basis for weighing molecules. Two equal volumes of gas (at the same temperature and pressure) are weighed. If we assume these two volumes contain the same numbers of molecules, then we must also conclude that the gas that weighs more must have heavier molecules. Furthermore, the ratio of the masses of the molecules must be the ratio of the masses of the two gas samples.

For example, in Table 1-1, page 6, data were given that show that 32.0 grams of oxygen at 0°C and one atmosphere pressure occupy 22.4 liters. The same volume of ammonia (also at 0°C and one atmosphere pressure) weighs 17.0 grams. By Avogadro's Hypothesis, these two volumes contain equal numbers of molecules. Each ammonia molecule must weigh less than an oxygen molecule by the factor 17.0/32.0. By the same argument, each hydrogen chloride molecule must weigh more than an oxygen molecule by 36.5/32.0.

By many such weighings, scientists have learned the relative masses of many gases. The experiment is fairly simple. A carefully measured volume of oxygen is weighed at a fixed pressure and temperature. Then the same volume of another gas is weighed, at the same pressure and temperature. The relative masses of the gas samples indicate the relative masses of the molecules. Neither the pressure nor the temperature need be measured, provided they are held constant.

Look at the sample data that would be obtained from such an experiment. The air is removed from a one-liter flask and the flask is weighed. In turn, the flask is filled with different gases and weighed again. (We must be sure that the temperature and pressure of the gases are the same in this experiment. The conditions chosen for this experiment are 25°C and one atmosphere pressure.) The experimental results are summarized in Table 2-4.

TABLE 2-4

Masses of One Liter of Gases at 25°C
and One Atmosphere Pressure

Gas	Mass of Flask Empty (grams)	Mass of Flask + Gas (grams)	Mass of One Liter of Gas (grams)	Mass of Molecule Relative to Oxygen
Oxygen	157.35	158.66	1.31	(32.0)
Ammonia	157.35	158.05	0.70	17.0
Hydrogen chloride	157.35	158.84	1.49	36.5
Nitrogen	157.35	158.50	1.15	28.0
Carbon dioxide	157.35	159.16	1.81	44.0
Nitrogen dioxide	157.35	159.23	1.88	46.0
Nitric oxide	157.35	158.58	1.23	30.0

EXERCISE 2-2

At 25°C and 1 atm pressure, one liter of neon gas weighs 0.83 gram. What is the mass of a neon molecule relative to the mass of an oxygen molecule (32.0) ?

2-4 The Number of Atoms in a Molecule

Recall the reaction between the two colorless gases, nitric oxide and oxygen. When nitric oxide reacts with oxygen, a reddish-brown gas forms. The color is identical to that of another gas, nitrogen dioxide. All the properties of the reddish-brown gas are consistent with the conclusion that nitrogen dioxide has been formed. How can this change be discussed in terms of our theory for gas behavior?

Since we find that nitrogen dioxide can be formed from the reaction of nitric oxide and oxygen, we can conclude that the atoms in nitrogen dioxide must have come from those in nitric oxide together with those in oxygen. Also, we find from an experiment that two volumes of nitric oxide combine with one volume of oxygen. Two volumes of nitrogen dioxide are formed. According to Avogadro's Hypothesis, these values for large samples indicate that:

$$\begin{matrix}\text{2 molecules}\\ \text{nitric oxide}\end{matrix} + \begin{matrix}\text{1 molecule}\\ \text{oxygen}\end{matrix} \longrightarrow \begin{matrix}\text{2 molecules}\\ \text{nitrogen dioxide}\end{matrix}$$

$$\boxed{\begin{matrix}\text{nitric}\\ \text{oxide}\end{matrix}} + \boxed{\text{oxygen}} \longrightarrow \boxed{\begin{matrix}\text{nitrogen}\\ \text{dioxide}\end{matrix}}$$

The oxygen molecule must have split into two equal parts. We can say "two" because two molecules of nitrogen dioxide are formed. We can say "equal" because all nitrogen dioxide molecules are alike. The oxygen molecule must contain an even number of atoms. In addition, no one has ever reported an experiment in which one volume of oxygen formed more than two volumes of an oxygen-containing compound. Chemists have concluded from this and other experiments that there are two oxygen atoms in an oxygen molecule.

EXERCISE 2-3

One volume of hydrogen gas reacts with one volume of chlorine gas to form two volumes of hydrogen chloride gas. What can you say about the number of atoms in one molecule of hydrogen? of chlorine? of hydrogen chloride?

The proposal that all matter consists of atoms is called the **Atomic Theory.** As with any explanation or theory, its value depends upon its usefulness in explaining experimental facts. The Atomic Theory was proposed in 1803 by an English chemist, John Dalton. We shall use it throughout this course. In Chapters 7 and 8 we shall review some of the experiments which have led chemists to regard the Atomic Theory as the cornerstone of their science.

2-5 Substances: Elements and Compounds

Molecules are clusters of atoms. Two types of molecules are possible. Some molecules are clusters of atoms in which all the atoms are identical. Other molecules contain two or more different kinds of atoms. Substances made of these two kinds of molecules are given different names.

> An **element** is a pure substance containing only one kind of atom.
>
> A **compound** is a pure substance containing two or more kinds of atoms.

There are over one hundred different elements known today. Some elements occur pure in nature and have been known for thousands of years. Elements like iron, silver, gold, mercury, and sulfur were known to the ancients. They were given Latin names by the early chemists. For example, iron was called **ferrum**, silver was called **argentum**, and gold was called **aurum**.

During the nineteenth century the number of elements discovered increased as chemists began to adopt quantitative methods. Twenty-five elements were known at the beginning of the nineteenth century. One hundred years later over 81 elements were known. More than twice as many elements were discovered in that one century as were discovered up to that time. Each element has a name and has been given a shorthand symbol of one or two letters. The element carbon is symbolized by the letter *C*, the element neon by the letters *Ne*. Ten of the elements have symbols derived from the capitalized first letter of the Latin name of the element and, if necessary, by a second letter. The ten include seven common metals known to the ancients. The symbol for the element tungsten comes from the German word *wolfram.* Except for the eleven elements listed in Table 2-5, all of the elements have symbols that can be derived from their English names. For example, the symbols for hydrogen (H), helium (He), carbon (C), nitrogen (N), oxygen (O), calcium (Ca), and chlorine (Cl) are easily obtained from the names. Notice that He is used for helium to distinguish it from H for hydrogen. Since C is used for carbon, the symbols for calcium and chlorine have a second letter added to the first. The table of elements, inside the back cover of the book, contains a complete list of the chemical symbols.

TABLE 2-5

Chemical Symbols That Are Not Derivable from the Common English Name of the Element

Common Name	Symbol	Symbol Source	Common Name	Symbol	Symbol Source
Antimony	Sb	stibium	Potassium	K	kalium
Copper	Cu	cuprum	Silver	Ag	argentum
Gold	Au	aurum	Sodium	Na	natrium
Iron	Fe	ferrum	Tin	Sn	stannum
Lead	Pb	plumbum	Tungsten	W	wolfram
Mercury	Hg	hydrargyrum			

But now consider a substance like water, which is probably the most familiar substance that we know. Water can be identified by its properties: color, taste, melting and boiling temperatures, and its ability to dissolve sugar and salt. A demonstration can easily show how water can be changed into two other substances, hydrogen gas and oxygen gas. The hydrogen and oxygen are produced in definite amounts. Since water can be decomposed into two other substances, water must contain at least two kinds of atoms. *Water is a compound.*

Sugar is another substance that you know. One property of sugar is its sweetness. Another property is that it dissolves in water. Still another is the way it behaves when heated. At a definite temperature sugar not only begins to melt to a liquid, but it also begins to decompose. The liquid darkens and water bubbles off. Finally, a black solid remains in the container. We recognize the black solid as a form of carbon, charcoal. Sugar can be decomposed to form water and charcoal in definite amounts. *Sugar is a compound.*

Water and sugar are compounds. What about hydrogen and oxygen? Hydrogen is a gas at normal conditions. It can be liquefied at a characteristic temperature by cooling. It becomes a solid at a second characteristic temperature. It is a pure substance. No treatment, however, causes it to form two other substances. Hydrogen then must contain only one kind of atom. *Hydrogen is an element.* Oxygen, too, has characteristic properties. It cannot be decomposed into two other substances. *Oxygen is an element.* It contains only one kind of atom.

Now we can return to the decomposition of water. Water can be decomposed to give hydrogen and oxygen. Since hydrogen contains only hydrogen atoms and oxygen contains only oxygen atoms, water molecules must contain some hydrogen atoms and some oxygen atoms, but no other kind of atom.

Finding what atoms are present in a given substance is one of the most important experiments in chemistry. How important this is can be seen by comparing the three substances water, oxygen, and hydrogen. Both water and oxygen contain oxygen atoms, but these substances are very different in their properties. Both water and hydrogen contain hydrogen atoms, but these substances are no more alike than are water and oxygen. The properties of water are fixed by the combination of the two kinds of atoms and these properties are distinctive.

EXERCISE 2-4

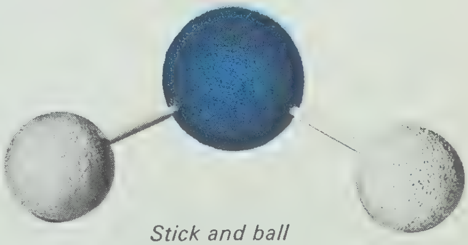
What differences between water, oxygen, and hydrogen can you point out from your own experience? For example, consider

(a) boiling and melting temperatures,
(b) role in combustion,
(c) role in supporting life.

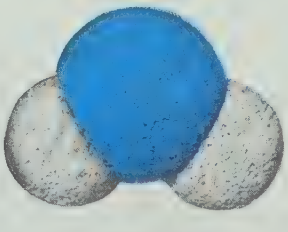
Sugar is another substance that contains both oxygen and hydrogen atoms, but it contains carbon atoms as well. The various types of atoms and their arrangement account for the distinctive properties which identify sugar. In any substance, the atoms present, their numbers, and their arrangement fix the properties of that substance.

2-6 Chemical Formulas

Molecules are made up of atoms in definite numbers and definite arrangements. Symbols for the elements aid us in showing the com-



Stick and ball model



Space filling model

FIGURE 2-6

Models to represent a water molecule.

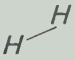
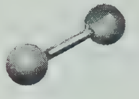
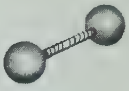
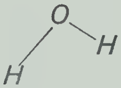
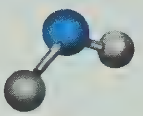
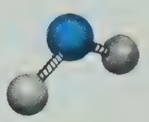
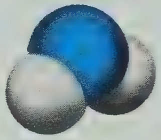
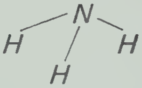
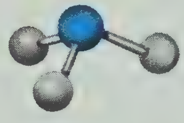
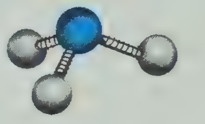
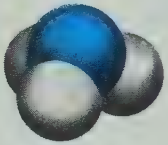
Name	Molecular Formula	Structure Formula	Models		
			Ball-and-Stick	Ball-and-Spring	Space-Filling
Hydrogen	H_2				
Water	H_2O				
Ammonia	NH_3				

FIGURE 2-7 Different representations of the molecules H_2, H_2O, and NH_3.

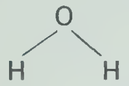
position of a molecule. Molecular models can, too. Figure 2-6 shows a model of a water molecule. Experiments have shown that the model should contain two atoms of hydrogen and one atom of oxygen. The model in Figure 2-6 shows the spatial arrangement of the atoms. In a water molecule each of the two hydrogen atoms is connected to the oxygen atom in a triangular arrangement. How the shape is determined and how important it is in chemistry will be discussed later.

The number and kinds of atoms in a molecule can also be shown in a **molecular formula.** For example, the water molecule is symbolized H_2O. In this molecular formula, H means a hydrogen atom, and O means an oxygen atom. The subscript following H indicates that there are two hydrogen atoms in the molecule for each oxygen atom. The molecular formula of ammonia, NH_3, indicates that one molecule of ammonia contains one atom of nitrogen (N) and three atoms of hydrogen (H). Experiments show that oxygen is diatomic. Each oxygen molecule contains two atoms. Its molecular formula is O_2. Hydrogen gas is diatomic. Its formula is H_2.

EXERCISE 2-5

Carbon dioxide has the formula CO_2. Remembering that the prefix "di" means two, and "tri" means three, write the formula for each of the following substances: carbon disulfide, sulfur dioxide, sulfur trioxide. (If you don't know the symbol for any element, use the table inside the back cover of the book.)

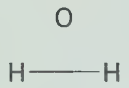
Both the numbers and the arrangment of the atoms in the molecule can be shown by a **structural formula.** Structural formulas, like the molecular models we have seen, show which atoms are attached to each other. Water has the structural formula



not

$H—H—O$

or

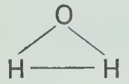


$\overset{\mathrm{O}}{\mathrm{H{-}{-}{-}H}}$

In the structural formula H—O—H, the lines indicate the connections between the atoms. The connections between atoms are called **chemical bonds.** We see that each hydrogen atom is bound to the oxygen atom. The alternate arrangements,

$H—H—O$

and



agree with the molecular formula H_2O. However, we know from experiments that the atoms are not bonded in these ways.

No written formula is quite as effective as a molecular model to help us visualize molecular shape. Since chemists find that the shape of a molecule strongly influences its chemical behavior, molecular models are important aids. Various molecular models are commonly used, depending upon the emphasis needed. Figure 2-7 shows some representations of molecules of hydrogen, water, and ammonia. The ball-and-stick and ball-and-spring models display clearly the atoms and their bonds. The space-filling models provide a more realistic view of the spatial relationships and crowding among nonbonded atoms.

2-7 The Mole

Whenever you weigh a substance or whenever you measure the volume of a gas, your sample contains a very large number of atoms. Chemists have found it convenient to choose a unit much larger than a single atom or molecule for comparing amounts of different materials. This unit, called the *mole,* contains a very large number of particles, 6.0×10^{23}. A mole of oxygen atoms, or a mole of hydrogen atoms, or a mole of copper atoms contains 6.0×10^{23} atoms of the specified kind. A mole of oxygen molecules, O_2, contains 2 moles of oxygen atoms [2 × (6.0×10^{23}) oxygen atoms] because each oxygen molecule contains two atoms. Chemists know that the molecular formula for phosphorus is P_4. There are four atoms in each molecule. A mole of P_4 molecules contains [4 × (6.0×10^{23})] phosphorus atoms, that is, four moles of phosphorus atoms.

A baker counts biscuits in dozens, a convenient number. Money is counted in dollars. How did chemists choose to count in terms of moles? The number 6.0×10^{23} seems an odd choice. There is a reason. Chemists prefer a definition in terms of a quantity that can be measured readily and with high precision. Weighing is much easier than counting when the number of particles is so very large. Consequently, chemists based the definition of the mole upon a chosen mass rather than a chosen number of particles. During the nineteenth century, chemists decided that the number of molecules in a sample of oxygen gas weighing exactly 32 grams would be taken as the standard number.* A mole was defined as the number of oxygen molecules in thirty-two grams of oxygen gas. The significance of a mole is most usefully connected with this number of particles, rather than the mass. The number 6.0×10^{23} is called **Avogadro's number.** This number occurs so many times in chemistry that it is often represented by the letter N. Do you see now why we chose to talk about 32.0 grams of oxygen in the pressure-volume example in the last chapter? In doing that we were dealing with one mole of oxygen molecules.

In 1961 and 1962, chemists and physicists agreed upon a new standard. The change is too small to affect our discussion.

Exercise 2-6

Since a mole of oxygen weighs 32.0 grams, how much would one million oxygen molecules weigh? Why was a mole not defined as one million molecules?

2-8 Molar Mass

Although a chemist knows that the mass of a single oxygen atom is 2.67×10^{-23} gram, he finds it much more convenient to know that a mole of oxygen atoms has a mass of 16.0 grams and that a mole of oxygen molecules has a mass of 32.0 grams. These amounts can be easily weighed in the laboratory. The mass of one mole of a substance is a useful number. We will call it the **molar mass.**

The **molar mass** of an element in the atomic state is the mass of *N atoms.*

There is a table inside the back cover of this book which lists the molar masses for elements in the atomic state. For example, O = 16.0 grams, Cu = 63.5 grams, and Ag = 107.9 grams.

---

* For molecules, O_2 = 32 grams was chosen as the standard mass. Therefore for atoms, O = 16 grams became the standard mass.

The **molar mass** of a compound or of an element in the molecular state is the mass of *N molecules*.

A chemist working with hydrogen chloride often needs to know its molar mass. This mass can be calculated from the molar masses of the two kinds of atoms, H and Cl.

one molecule of HCl	contains	one atom of hydrogen	and	one atom of chlorine
one mole of HCl molecules	contains	one mole of hydrogen atoms	and	one mole of chlorine atoms
the mass of one mole of HCl molecules	is the same as	the mass of one mole of hydrogen atoms	+	the mass of one mole of chlorine atoms
molar mass of HCl	=	molar mass of atomic hydrogen	+	molar mass of atomic chlorine
molar mass of HCl	=	1.01 g	+	35.5 g
molar mass of HCl	=	36.5 g		

If we know the molecular formula for a substance, we can calculate its molar mass. This mass contains 6.0×10^{23} molecules, one mole of molecules.

EXERCISE 2-7

Show that the mass of a mole of NO_2 is 46.0 grams and that the mass of a mole of SO_2 is 64.1 grams.

EXERCISE 2-8

What is the molar mass of each of the following substances: sulfur (formula, S_8); ammonia (formula, NH_3); and nitrogen (a diatomic molecule)?

EXERCISE 2-9

Calculate the mass of 6.0×10^{23} molecules of carbon monoxide, CO.

2-9 Calculations Based on the Mole

If we take a certain mass of a substance, we can calculate the number of moles that we have of that substance. We can also calculate how many molecules we have. Here is an example to help you understand these calculations.

How many moles and how many molecules are contained in 2.2 grams of carbon dioxide? The molecular formula CO_2 tells us that its molar mass is the mass of one mole of C atoms plus the mass of two moles of O atoms.

$$\begin{aligned}\text{Molar mass of } CO_2 &= \text{molar mass of C} + (2 \times \text{molar mass of O}) \\ &= 12.0 + (2 \times 16.0) \\ &= 44.0 \text{ grams}\end{aligned}$$

In our example, we have taken a smaller mass than 44.0 grams. We have less than 1.0 mole. If we have taken less than 1.0 mole of carbon dioxide, then we should have fewer than 6.0×10^{23} molecules. We will use these guides to check our answers.

$$\begin{aligned}\text{Number of moles of } CO_2 &= \frac{\text{mass of } CO_2}{\text{molar mass of } CO_2} \\ &= \frac{2.2 \text{ grams}}{44.0 \text{ grams/mole}} \\ &= 0.050 \text{ mole}\end{aligned}$$

An important aid in working numerical problems is found in writing words or units after each number to tell what each number measures. Just as numbers can be combined, so can units. We have two very quick checks on our problem solving. The first was our guess that the answer would be less than 1.0 mole. Our answer 0.050 mole confirms our guess. The second check comes from combining units to give an answer which has the units asked for in the problem. We can write out the units to show how the combination takes place.

$$\frac{\text{grams}}{\text{grams/mole}} \quad \text{is the same as}$$

$$\text{grams} \times \frac{1}{\text{grams/mole}}$$

or

$$\text{grams} \times \frac{\text{mole}}{\text{grams}}$$

or

$$\text{mole}$$

Now let us find out how many molecules we have in 2.2 grams of CO_2. We will use units to check our calculation.

$$\begin{aligned}\text{Number of molecules of } CO_2 &= \text{number of moles of } CO_2 \times \frac{\text{number of molecules}}{\text{mole}} \\ &= 0.050 \text{ mole} \times 6.0 \times 10^{23} \text{ molecules/mole} \\ &= 3.0 \times 10^{22} \text{ molecules}\end{aligned}$$

This number is less than 6.0×10^{23}, which agrees with our guess of the answer.

EXERCISE 2-10

How many moles of iron atoms are present in 1.67 grams of iron? How many iron atoms are present in 1.67 grams of iron?

If a chemist knows the relative masses of the elements in a compound, he can calculate the **empirical formula** for the substance. The empirical formula gives only the relative number of each kind of atom in the compound. Let us look at an example. A chemist has made 32.0 grams of a compound called hydrazine. Chemical analysis shows there are 28.0 grams of nitrogen and 4.0 grams of hydrogen in this compound. What is the empirical formula for hydrazine?

In a problem like this, we want to compare the number of atoms of nitrogen with the number of atoms of hydrogen. This comparison is easy to carry out if we calculate the number of moles of each element first.

$$\begin{aligned}\text{Number of moles of N atoms} &= \frac{\text{mass of nitrogen}}{\text{molar mass of N atom}} \\ &= \frac{28.0 \text{ grams}}{14.0 \text{ grams/mole}} \\ &= 2.0 \text{ moles}\end{aligned}$$

$$\begin{aligned}\text{Number of moles of H atoms} &= \frac{\text{mass of hydrogen}}{\text{molar mass of H atom}} \\ &= \frac{4.0 \text{ grams}}{1.0 \text{ gram/mole}} \\ &= 4.0 \text{ moles}\end{aligned}$$

If we multiplied each of these numbers by 6.0×10^{23}, we would find the number of N atoms and the number of H atoms. Since we want to find the relative number of each kind of atom, we can compare the number of moles directly.

$$\frac{\text{Number of H atoms}}{\text{Number of N atoms}} = \frac{\text{moles of H atoms}}{\text{moles of N atoms}} = \frac{4.0 \text{ moles H atoms}}{2.0 \text{ moles N atoms}} = 2.0$$

This last ratio is often called the **mole ratio.** The mole ratio in hydrazine is 2.0 H atoms for every N atom. We can write the **empirical formula** for this substance as (NH_2). The molecular formula for the substance hydrazine is different from the empirical formula. In later chapters we will discuss methods to establish the molecular formula for a compound. The molecular formula for hydrazine is known to be N_2H_4. Notice the mole ratio for the molecule is 2 H for every N atom.

EXERCISE 2-11

A compound contains 6.0 grams of carbon for each 2.0 grams of hydrogen. Convince yourself that the empirical formula is CH_4 for this compound.

2-10 Review

The explanation for the regularity in gas behavior, PV = a constant, in terms of molecular particles is called a **theory.** We make use of a **model system,** ball bearings shaken in a box, in arriving at this explanation. In this chapter we have seen the theory grow.

Gases differ in properties like color, odor, and solubility in water. The masses of molecules of different gases also are different. The idea that equal volumes of gases (at the same temperature and pressure) contain equal numbers of molecules is called **Avogadro's Hypothesis.** This proposal offers a simple explanation for the integral ratios observed for the reacting volumes of different gases. Moreover, this idea leads to an experimental method for measuring the relative masses of molecules of different gases.

Chemists have found it useful to choose a particular number of molecules, 6.0×10^{23}, as the unit in comparing one substance with another. This number is called **Avogadro's Number, *N*.** Chemists use the word **mole** when referring to 6.0×10^{23} particles.

In the nineteenth century the value 32.0 grams was chosen for the mass of one mole of oxygen molecules. Since the oxygen molecule is diatomic, the molar mass of atomic oxygen is 16.0 grams. The molar mass for atoms of other elements can be established by comparison with the molar mass of atomic oxygen.

In the next chapter we will see how important the idea of the mole can be when we begin to study chemical reactions.

Questions and Problems for Chapter 2

1

How could you make money buying argon gas at $1.00 per liter and selling it for $0.50 per liter?

2

Four differences between helium gas and nitrogen gas are listed below.

(a) Dry air contains 80% nitrogen but only 0.0005% helium (by volume).
(b) Helium is much less dense than nitrogen.
(c) Helium has much lower solubility in water than nitrogen has.
(d) Helium is much more expensive than nitrogen.

Which difference could account for the fact that a deep-sea diver is much less likely to suffer from the bends if he breathes a mixture of 80% helium and 20% oxygen than if he breathes air? (The bends is a painful, sometimes fatal, condition caused by the formation of gas bubbles in the veins and consequent interruption of blood flow. The bubbles form from gas dissolved in the blood at high pressure.)

3

The most important step in the process for conversion of atmospheric nitrogen into important commercial compounds used for fertilizers or explosives involves the combination of one volume of nitrogen gas with three volumes of hydrogen gas to form two volumes of ammonia. From these data alone and Avogadro's Hypothesis, how many molecules of hydrogen combine with one molecule of nitrogen? How many molecules of ammonia are produced for each molecule of nitrogen used?

4

Gaseous uranium hexafluoride is important in the preparation of uranium as a source of "atomic energy." A flask filled with this gas is weighed under certain conditions of temperature and pressure. The mass of the gas is found to be 3.52 grams. The same flask is filled with oxygen gas and is weighed under the same conditions. The mass of the oxygen is found to be 0.32 gram.

(a) What is the ratio of the mass of one uranium hexafluoride molecule to the mass of an oxygen molecule?
(b) State any guiding principles needed in answering the question.

5

A white substance, on heating, forms a colorless gas and a purple solid. Is the substance an element or a compound? Why?

6

What do the following symbols represent? K, Ca, Co, CO, Pb, Hf, HF.

7

Here are the names of some common chemicals and their formulas. What elements does each compound contain?

(a) hydrogen peroxide	H_2O_2
(b) jeweler's rouge	Fe_2O_3
(c) light bulb filament	W
(d) tetraethyl lead	$Pb(C_2H_5)_4$
(e) baking soda	$NaHCO_3$
(f) octane	C_8H_{18}
(g) household gas	CH_4

8

For each of the following substances, give the name of each kind of atom present and the total number of atoms represented in the formula.

Name	Formula
(a) graphite (pencil lead)	C
(b) diamond	C
(c) sodium chloride (table salt)	NaCl
(d) sodium hydroxide (lye)	NaOH
(e) calcium hydroxide	$Ca(OH)_2$
(f) potassium nitrate	KNO_3
(g) magnesium nitrate	$Mg(NO_3)_2$
(h) sodium sulfate	Na_2SO_4
(i) calcium sulfate	$CaSO_4$

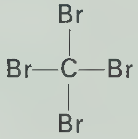
9

All of the following substances are called "acids." What element do they have in common?

(a) nitric acid	HNO_3
(b) hydrochloric acid	HCl
(c) acetic acid	$HC_2H_3O_2$
(d) sulfuric acid	H_2SO_4
(e) phosphoric acid	H_3PO_4

10

What does the molecular formula CBr_4 mean? What additional information is provided by the structural formula?



$$\begin{array}{c} Br \\ | \\ Br{-}C{-}Br \\ | \\ Br \end{array}$$

11

Write formulas for these compounds.

silicon dioxide
sulfur dichloride
nitrogen trifluoride
aluminum trifluoride
dinitrogen difluoride

12

Write formulas for these compounds.

hydrogen chloride
hydrogen bromide
hydrogen iodide
boron trichloride
carbon tetrachloride
nitrogen trichloride
oxygen dichloride

13

How many particles are there in a mole?

14

How many moles of oxygen atoms are in one mole of nitric acid molecules? Of sulfuric acid molecules?

15

If we had one mole of pennies to divide among all the people in the world, how many dollars would each of the three billion inhabitants receive?

16

How many moles of people are there on earth?

17

If there were a mole of people evenly distributed over the surface of the earth, including both land and sea, how many square inches would be allotted to each person?

18

What is the mass in grams of one silver atom?

19

A liter of chlorine gas is 2.22 times as heavy as a liter of oxygen gas when both are measured at room temperature and pressure. Calculate the molar mass of chlorine. How does this value compare with the molar mass of atomic chlorine, found in the table of molar masses? What is the formula of a molecule of chlorine?

20

Suppose chemists had chosen a billion billion (10^{18}) as the number of particles in one mole. What would the molar mass for molecular oxygen be?

21

If $1\frac{1}{2}$ moles of hydrogen gas (H_2) react in a given experiment, how many grams of hydrogen does this represent?

22

Calculate the molar mass for each of these substances: SiF_4, HF, Cl_2, Xe, NO_2.

23

Write the formulas for these compounds and give the mass of one mole of each.

carbon disulfide
sulfur hexafluoride
nitrogen trichloride
osmium tetroxide

24

Consider the following data:

Element	Molar mass of atoms
A	12.01
B	35.5

A and *B* combine to form a new substance, *X*. If four moles of *B* combine with one mole of *A* to give one mole of *X*, then the mass of one mole of *X* is:

(a) 47.5 grams
(b) 74.0 grams
(c) 83.0 grams
(d) 154.0 grams
(e) 166.0 grams

25

A flask of gaseous CCl_4 was weighed at a measured temperature and pressure. The flask was flushed and filled with oxygen at the same temperature and pressure. The mass of the CCl_4 vapor will be about:

(a) the same as that of oxygen.
(b) one-fifth as heavy as the oxygen.
(c) five times as heavy as the oxygen.
(d) twice as heavy as the oxygen.
(e) one-half as heavy as the oxygen.

26

In Experiment 5 you calculated the ratio of the mass of carbon dioxide to the mass of the same volume of oxygen. Molecular oxygen has been assigned a molar mass of 32.0 grams. From the molar mass of oxygen and your measured ratio, calculate the molar mass of carbon dioxide. Estimate the uncertainty in your result. Compare the value you obtain with the molar mass of CO_2 calculated on page 34.

27

A glass bulb weighs 108.11 grams after all of the gas has been removed from it. When filled with oxygen gas at atmospheric pressure and room temperature, the bulb weighs 109.56 grams. When filled, at the same pressure and temperature, with a gas sample obtained from the mouth of a volcano, the bulb weighs 111.01 grams. Which of the following molecular formulas for the volcano gas could account for the data?

CO_2
OCS
Si_2H_6
SO_2
NF_3
SO_3
S_8
A gas mixture, half CO_2 and half Kr.

28

A chemist weighs out 10.0 grams of water, 10.0 grams of ammonia, and 10.0 grams of hydrogen chloride. How many moles of each substance does he have?

29

How many moles of atoms are there in 9.0 grams of aluminum? In 0.83 gram of iron?

30

How many moles are there in 49 grams of H_2SO_4?

31

The most delicate balance can detect a change of about 10^{-8} gram. How many atoms of gold would there be in a sample of that mass?

32

A stone about the size of a softball weighs roughly one kilogram. How many moles of such stones would be needed to account for the entire mass of the earth, about 6×10^{27} grams?

33

How many atoms are in a copper penny (mass 2 grams)?

34

How many grams of table sugar ($C_{12}H_{22}O_{11}$) are needed to supply one molecule for each of the 3×10^9 people on earth?

35

Acetylene gas is used in welding. Acetylene contains 30 grams of carbon for each 2.5 grams of hydrogen. What is the empirical formula for acetylene?

36

There are two common oxides of sulfur. One contains 32 grams of sulfur for each 32 grams of oxygen. The other oxide contains 32 grams of sulfur for each 48 grams of oxygen. What are the empirical formulas of these oxides?

37

A variety of phosphorus called red phosphorus is used in match heads. It burns to produce an oxide, 0.142 gram of the oxide containing 0.062 gram of phosphorus. What is the empirical formula of this oxide?

38

There are two known compounds containing only tungsten and carbon. One is the very hard alloy, tungsten carbide, used for the edges of cutting tools. Analysis of the two compounds gives, for one, 1.82 grams of tungsten per 0.12 gram of carbon, and for the other compound, 3.70 grams of tungsten per 0.12 gram of carbon. What are the empirical formulas for these compounds?

39

Equal volumes of oxygen and gas *A* are compared at the same temperature and pressure.

The mass of oxygen = 0.64 gram
The mass of gas *A* = 3.42 grams

(a) Calculate the molar mass for gas *A*.
(b) Given the empirical formula for gas *A*, CF_2Cl, what is the molecular formula for this gaseous substance?

40

Gas *A*, a compound containing nitrogen and oxygen, was compared to gas *B* in an experiment. Equal volumes of gas *A* and gas *B* are compared at the same temperature and pressure.

Mass of gas *A*	0.56 gram
Mass of gas *B*	0.30 gram
Molar mass of gas *B*	16.0 grams

(a) Which of these oxides of nitrogen is gas *A*? N_2O, NO, NO_2, N_2O_3, N_2O_5.
(b) Gas *B* is a compound containing only carbon and hydrogen. What is the molecular formula for gas *B*?

41

In Problem 40(a), the formulas for five different nitrogen oxides are listed. For each of these, calculate the oxygen to nitrogen mass ratio, $\frac{\text{g oxygen}}{\text{g nitrogen}}$. Show that these ratios are themselves in the ratio of small whole numbers. What does this tell you about the mass of oxygen for a fixed mass of nitrogen in these compounds? This regularity is sometimes called the **Law of Multiple Proportions.**

42

In addition to water, hydrogen and oxygen form a compound called hydrogen peroxide, H_2O_2. Calculate the ratio of grams of oxygen to grams of hydrogen for one mole of these two compounds. Compare the relative masses of oxygen in these two compounds. Does this comparison illustrate the **Law of Multiple Proportions?**

Principles of Chemical Reactions

3

You have studied several chemical reactions in the experiments that you have performed in the laboratory for this course. A candle burning in air produces carbon dioxide and water. Copper wire reacts with a solution of silver nitrate to form metallic silver. Aluminum metal dissolves in a copper chloride solution. Chemical changes are taking place in each of these experiments.

We don't have to be in a laboratory to observe chemical reactions. There are many occurring around us every day. Gasoline is burned in an automobile engine to provide energy to make the automobile move. Growing plants convert carbon dioxide and water into complex chemical substances and release oxygen to the atmosphere. Chemical reactions take place in the dry cells of a flashlight. When we push the flashlight button down, a beam of light is produced. Important structural materials like aluminum and steel are produced through chemical reactions. Drugs like penicillin and synthetic fibers such as nylon are known to all of us. These, and hundreds of other substances, are examples of important substances made through chemical reactions.

A chemist wants to understand and control chemical reactions. In this chapter we will examine some simple ones. We will find that certain principles apply in any chemical reaction that is studied. Suppose we begin with a reaction that forms a familiar substance, water.

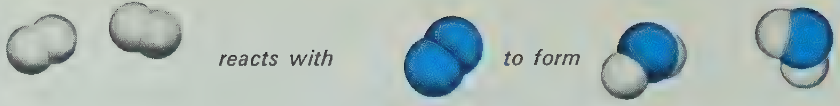
3-1 Formation of Water from Hydrogen and Oxygen

Water is produced when two volumes of hydrogen gas combine with one volume of oxygen gas. The properties of water are very different from the properties of the starting materials, hydrogen and oxygen.

Try to imagine what is happening at the molecular level. We begin with hydrogen and oxygen molecules. Water molecules form in the reaction. For this to happen the bonds between atoms in the reacting substances are broken. New bonds form as the atoms rearrange to give water molecules. Molecular models help us picture this change.

FIGURE 3-1
Molecular models

$2\,H_2 + O_2 \longrightarrow 2\,H_2O$



Two hydrogen molecules and one oxygen molecule are represented on the left of Figure 3-1. When these molecules react to form water, the bonds between the atoms in the oxygen molecule and in the hydrogen molecules must be broken. As water molecules form, the molecular models show clearly that new chemical bonds form. A chemical change has taken place. Although the atoms regroup to form two water molecules, the total number of atoms does not change.

EXERCISE 3-1

Suppose ten hydrogen molecules and ten oxygen molecules are mixed. How many molecules of water could be formed? What would be left over?

EXERCISE 3-2

One million oxygen molecules react with sufficient hydrogen molecules to form water molecules. How many water molecules are formed? How many hydrogen molecules are required?

Production of 100 water molecules requires 100 hydrogen molecules to react with 50 oxygen molecules. We would need 6.0×10^{23} hydrogen molecules to react with 3.0×10^{23} oxygen molecules to produce 6.0×10^{23} water molecules.

To make one mole of water, one mole of hydrogen gas must react with one-half mole of oxygen gas.

These results are summarized in Table 3-1.

TABLE 3-1

Reacting Amounts of Hydrogen and Oxygen to Form Water

Hydrogen	Oxygen (In numbers of molecules)	Water
2	1	2
100	50	100
6.0×10^{23}	3.0×10^{23}	6.0×10^{23}
	(In number of moles)	
1	$\frac{1}{2}$	1
2	1	2
10	5	10

If one mole of hydrogen gas reacts with one-half mole of oxygen gas at 25°C, one mole of liquid water is produced. A large amount of heat energy is given off during this reaction. The quantity of heat energy produced when one mole of liquid water is formed is 68,300 calories. (A **calorie** is the unit of heat energy that chemists use. It is the amount of heat energy needed to raise the temperature of one gram of water 1C°.) Two moles of hydrogen react with one mole of oxygen. Two moles of water would be produced and 2 × 68,300 calories, or 136.6 kilocalories, of heat energy would be released.

This heat energy must come from the reactants, hydrogen and oxygen, since no heat energy was supplied from the outside after the reaction started. We may conclude that water has less energy than the reactants used to make it. A chemical reaction in which energy is released is called an **exothermic reaction.**

If we mix hydrogen gas with oxygen gas and then ignite the mixture with a spark, a violent explosion results. Even so, the quantity of water produced is the same, per mole of hydrogen gas reacting, as in controlled burning.

EXERCISE 3-3

How much heat energy is released when ten moles of hydrogen gas burn? One-tenth mole?

3-2 Decomposition of Water

We can decompose the water in a solution of water and sulfuric acid by passing an electric current through the solution. The way to do this is shown in Figure 3-2. Two pieces of metal called electrodes are placed in the solution. When the electrodes are connected to a source of electrical energy, hydrogen gas appears at one electrode and oxygen gas at the other. If we operate the apparatus until one mole of water has decomposed, one mole of hydrogen gas and one-half mole of oxygen gas are produced. Electrical energy causes the decomposition of water. If energy is absorbed in a chemical reaction, we call it an **endothermic reaction.**

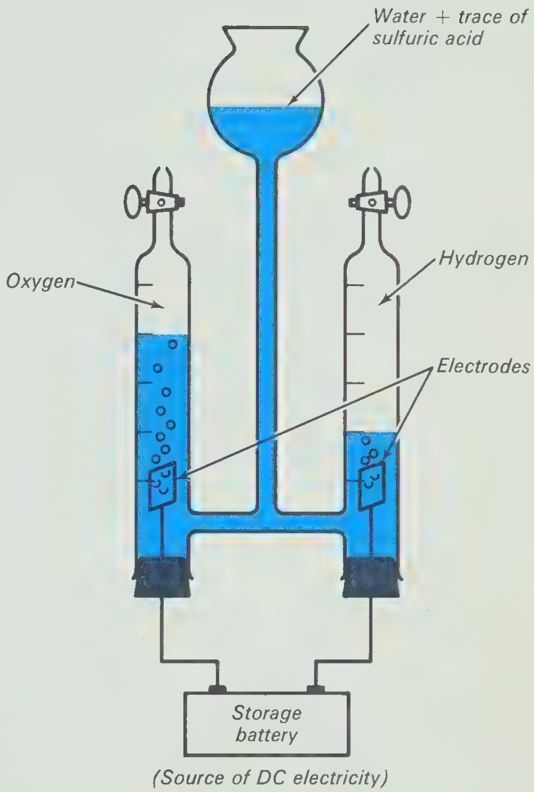


FIGURE 3-2

Electrolytic decomposition of water.

Let us compare the formation and decomposition of water. We can show with molecular models, Figure 3-3, that the chemical change in the formation of water is exactly the reverse of the chemical change in water decomposition. Simple rules describe these changes. In each drawing we find two oxygen atoms on the left and two oxygen atoms on the right. We can see four hydrogen atoms on the left and four on the right. Atoms are neither gained nor lost. Atoms are conserved in chemical reactions.

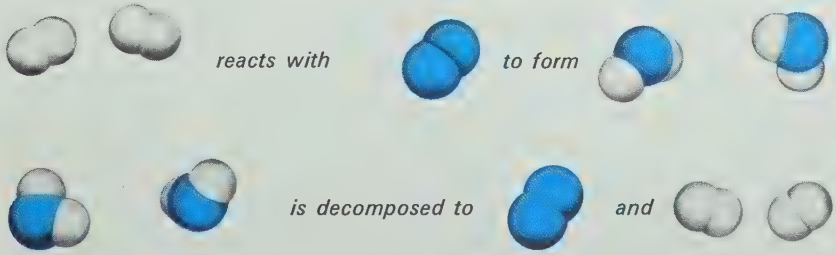


FIGURE 3-3

Molecular models

$2\,H_2O \longrightarrow 2\,H_2 + O_2$

3-3 Conservation of Mass

Belief in the conservation of atoms is based upon a generalization that has stood the test of many experiments. There is no detectable increase or decrease in the quantity of matter during a chemical change. Since we often measure a quantity of matter in terms of its mass, we may say that mass is conserved. One mole of liquid water weighs 18.0 grams. When this amount of water is decomposed, 2.0 grams of hydrogen and 16.0 grams of oxygen are produced:

1 mole of water, H_2O	→	1 mole of hydrogen, H_2	+	$\frac{1}{2}$ mole of oxygen, O_2
18.0 g	→	2.0 g	+	16.0 g
18.0 g reactants	give	18.0 g products		

In chemical reactions:

Matter is conserved.
Atoms are conserved.
The mass of the reactants is
equal to the mass of the products.

The number of moles of molecules may not be conserved in chemical reactions. We can understand this by recognizing that molecules undergo change or rearrangement in a chemical reaction. In our example of water decomposition

1 mole reactants	→	$1\frac{1}{2}$ moles product

Moles of molecules are not necessarily conserved in a chemical reaction.

3-4 Equations for Chemical Reactions

The molecular models we have used in representing chemical reactions help us visualize the rearrangement of atoms in the reactions. By a slight change we can show the results in a less detailed but simpler way. Chemical formulas can be used rather than drawings of the atoms and molecules. The formula of hydrogen is H_2, the formula of oxygen is O_2, and the formula of water is H_2O. By using the formulas to represent the molecules, we can write:

$$2\,H_2 + 1\,O_2 \longrightarrow 2\,H_2O$$
$$4\,H_2 + 2\,O_2 \longrightarrow 4\,H_2O$$
$$2\,H_2O \longrightarrow 1\,O_2 + 2\,H_2$$

Such expressions are called **chemical equations.** Notice that we show two molecules of a substance by writing the coefficient 2 before the formula. The coefficient 2 before the formula H_2O means two molecules of water. In two molecules of water, there are four hydrogen atoms and two oxygen atoms. Notice also that we can change the first equation into the second by doubling all the coefficients. We can change the first equation into the third equation by writing it in the opposite direction.

In all chemical equations, atoms are conserved. Every symbol, when multiplied by the subscript after it and the coefficient before the formula, must appear as often on the left side of the equation as on the right.

Let us consider another example. Natural gas contains a large amount of methane, CH_4. The chemical equation for methane burning in oxygen is:

$$1\ CH_4 + 2\ O_2 \longrightarrow 1\ CO_2 + 2\ H_2O$$

There is the same number of each kind of atom in the reactants and in the products. One carbon atom, four hydrogen atoms, and four oxygen atoms are represented on each side of the equation. Because of the relationship between a molecule and a mole, we can read this equation in two ways:

One molecule of methane + two molecules of oxygen ⟶
one molecule of carbon dioxide + two molecules of water.

or

One mole of methane + two moles of oxygen ⟶
one mole of carbon dioxide + two moles of water.

3-5 Writing Equations for Reactions

Let us practice writing equations for chemical reactions. First, we have to know what the reactants and products are. Then we follow two simple principles.

(1) We have to be able to write the correct molecular formula for each reactant and each product.
(2) We must show conservation of atoms.

Consider the reaction for the burning of magnesium to form magnesium oxide. The formulas needed are O_2, Mg, and MgO. When writing chemical equations, we write the formulas for the reactants on the left and the formulas for the products on the right:

$$Mg + O_2 \longrightarrow MgO$$

In order to conserve atoms, we must find numerical coefficients to place before each correct formula to obtain the same number of atoms of each element on the left side of the equation as there are on the right. The process of finding these coefficients is called *balancing the equation.*

First, suppose one mole of oxygen gas is consumed in the reaction.

$$Mg + 1\,O_2 \longrightarrow MgO$$

One mole of oxygen gas, with its two moles of oxygen atoms, forms two moles of magnesium oxide.

$$Mg + 1\,O_2 \longrightarrow 2\,MgO$$

But two moles of magnesium oxide require two moles of magnesium metal.

$$2\,Mg + 1\,O_2 \longrightarrow 2\,MgO$$

Atoms are conserved in the last statement; the equation is balanced.

We could have decided to begin balancing the equation by choosing one mole of magnesium metal as the amount of reactant consumed in the reaction.

Suppose one mole of magnesium is consumed in the reaction.

$$1\,Mg + O_2 \longrightarrow MgO$$

One mole of magnesium will form one mole of magnesium oxide.

$$1\,Mg + O_2 \longrightarrow 1\,MgO$$

One mole of magnesium oxide contains one mole of oxygen atoms, the number in one-half mole of oxygen molecules.

$$1\,Mg + {}^1\!/_2\,O_2 \longrightarrow 1\,MgO$$

This statement is also a balanced chemical equation. Atoms are conserved.

Either way of writing the chemical equation for the burning of magnesium is acceptable.

$$2\,Mg + 1\,O_2 \longrightarrow 2\,MgO$$

$$1\,Mg + {}^1\!/_2\,O_2 \longrightarrow 1\,MgO$$

We can multiply all of the coefficients in the second equation by 2 to obtain the first equation. We can always multiply or divide all coefficients in a balanced chemical equation by the same number and obtain an equally valid equation. In writing equations we often drop the coefficient 1, but it is never wrong to write it in the equation.

This example shows you that it does not matter where you start in balancing a chemical equation. The important thing is that you start! A few more examples will help you learn to balance equations.

Hydrogen gas, H_2, and chlorine gas, Cl_2, react to form hydrogen chloride gas, HCl.

Suppose we assume one mole of H_2 reacts. Conservation of hydrogen atoms requires that two moles of HCl be produced.

$$1\,H_2 + Cl_2 \longrightarrow 2\,HCl$$

There are two moles of chlorine atoms in the product, hydrogen chloride. One mole of Cl_2 is required.

$$1\ H_2 + 1\ Cl_2 \longrightarrow 2\ HCl$$

or

$$H_2 + Cl_2 \longrightarrow 2\ HCl$$

Formaldehyde has the molecular formula, H_2CO. Formaldehyde reacts with oxygen to form carbon dioxide and water. What is the equation for this reaction? Let us start with one mole of formaldehyde. One mole of carbon atoms, and two moles of hydrogen atoms, must appear in the products. We can write

$$1\ H_2CO + y\ O_2 \longrightarrow 1\ CO_2 + 1\ H_2O$$

Notice that we have not yet determined the coefficient of O_2. We have designated it as y to remind ourselves of this. Oxygen atoms must be conserved. Since three moles of oxygen atoms appear in the products of this reaction, three moles of oxygen atoms must have been present in the reactants. One mole of oxygen atoms can be counted in one mole of formaldehyde. Two more moles of oxygen atoms must be supplied by molecular oxygen. Since oxygen is a diatomic molecule, y must be equal to 1.

$$1\ H_2CO + 1\ O_2 \longrightarrow 1\ CO_2 + 1\ H_2O$$

or

$$H_2CO + O_2 \longrightarrow CO_2 + H_2O$$

EXERCISE 3-4

Ammonia, NH_3, reacts with oxygen, O_2, to give nitrogen, N_2, and water, H_2O. Follow the logic of each step in balancing this reaction.

$$NH_3 + O_2 \longrightarrow N_2 + H_2O$$
$$NH_3 + O_2 \longrightarrow 1\ N_2 + H_2O$$
$$2\ NH_3 + O_2 \longrightarrow 1\ N_2 + H_2O$$
$$2\ NH_3 + O_2 \longrightarrow 1\ N_2 + 3\ H_2O$$
$$2\ NH_3 + {}^3\!/_2\ O_2 \longrightarrow 1\ N_2 + 3\ H_2O$$

State briefly what was done in each step.

EXERCISE 3-5

A paraffin candle burns in air to form water and carbon dioxide. Paraffin is made up of molecules of several sizes. We shall use the molecular formula $C_{25}H_{52}$ as representative of the molecules present.

Formulas of Reactants		Formulas of Products
$C_{25}H_{52} + O_2$	$\longrightarrow$	$H_2O + CO_2$

Suppose one mole of paraffin is burned. We can write

(Exercise 3-5 continued on p. 48.)

(Exercise 3-5 continued from p. 47.)

$$1\ C_{25}H_{52} + y\ O_2 \longrightarrow 26\ H_2O + 25\ CO_2$$

We still have not determined the coefficient for O_2. Since 76 O atoms are required for the products $[26 + (2 \times 25) = 76]$, they must have been present in the reactants. Show that y must be 38:

$$C_{25}H_{52} + 38\ O_2 \longrightarrow 26\ H_2O + 25\ CO_2$$

Usually it is more useful to think of equations in terms of moles rather than molecules. A molar mass can be easily weighed. In the reaction represented by the equation

$$2\ Mg + O_2 \longrightarrow 2\ MgO$$

two moles of magnesium weighing 48.6 grams react with one mole of oxygen weighing 32.0 grams. Two moles of magnesium oxide weighing 80.6 grams are produced. Mass is conserved:

$$48.6 \text{ grams} + 32.0 \text{ grams} = 80.6 \text{ grams}$$

Notice that moles of molecules are *not* conserved in this reaction. Moles of atoms are conserved.

3-6 Calculations Based on Chemical Equations

Balanced equations give us the information we need for computing the masses of the substances consumed or produced in chemical reactions.

Suppose we wish to know how many moles of water are produced when 68 grams of ammonia are burned. We balanced the equation for this reaction in Exercise 3-4.

$$2\ NH_3 + {}^3/_2\ O_2 \longrightarrow N_2 + 3\ H_2O$$

The molar mass of ammonia is 17 grams. In this problem, 68 grams of NH_3 are burned. How many moles of NH_3 is this?

$$\frac{68 \text{ grams } NH_3}{17 \text{ grams/mole}} = 4.0 \text{ moles } NH_3$$

The balanced equation tells us that

$$2 \text{ moles } NH_3 \longrightarrow 3 \text{ moles } H_2O$$

This must mean that

$$4 \text{ moles } NH_3 \longrightarrow 6 \text{ moles } H_2O$$

We see that 68 grams, or four moles, of ammonia produce 6 moles of water. Since the molar mass for water is 18.0 grams, 6 × 18.0 or 108 grams of water would be formed.

Let us review the steps we follow in this calculation.

First, we balance the chemical equation.

Second, we calculate the number of moles of ammonia that reacted. To do this, divide the mass of ammonia by the molar mass for ammonia

$$\text{Number of moles} = \frac{\text{mass}}{\text{mass of 1 mole}} = \frac{\text{mass}}{\text{molar mass}}$$

$$\text{Number of moles of ammonia} = \frac{68 \text{ grams } NH_3}{17 \text{ grams/mole}} = 4.0 \text{ moles } NH_3$$

Third, we can read from the balanced equation the relationship between moles of water and moles of ammonia. From this relationship we can determine the number of moles of water that are produced from 4.0 moles of ammonia.

Fourth, we calculate the mass of water by reversing the operation in the second step.

$$\begin{aligned} \text{Mass} &= \text{Number of moles} \times \text{molar mass} \\ \text{Mass of } H_2O &= 6.0 \text{ moles} \times 18.0 \text{ grams/mole} \\ &= 108 \text{ grams } H_2O \end{aligned}$$

Another example will give us some practice in this kind of calculation. Suppose we want to know how much chlorine, Cl_2, is required to make 730 grams of hydrogen chloride, HCl. Let us follow the steps we have discussed.

First, balance the equation

$$H_2 + Cl_2 \longrightarrow 2\,HCl$$

Second, calculate the number of moles of HCl to be produced.

$$\text{number of moles HCl} = \frac{\text{mass HCl}}{\text{molar mass HCl}}$$

$$\text{number of moles HCl} = \frac{730 \text{ grams HCl}}{36.5 \text{ grams/mole}} = 20.0 \text{ moles HCl}$$

Third, from the balanced equation, read the relationship between number of moles of Cl_2 and the number of moles of HCl.

2 moles HCl can be made from 1 mole Cl_2.

20.0 moles HCl would require 10.0 moles Cl_2.

Fourth, calculate the mass of chlorine required.

$$\text{mass } Cl_2 = \text{number of moles } Cl_2 \times \text{molar mass } Cl_2$$

$$\text{mass } Cl_2 = 10.0 \text{ moles} \times 71.0 \text{ grams/mole} = 710 \text{ grams } Cl_2.$$

We would have to react 710 grams of chlorine with sufficient hydrogen to make 730 grams of hydrogen chloride.

EXERCISE 3-6

Show that 3.80 moles of oxygen are needed to burn 35.3 grams of paraffin by the reaction

$$C_{25}H_{52} + 38\ O_2 \longrightarrow 26\ H_2O + 25\ CO_2$$

EXERCISE 3-7

How many moles of oxygen, O_2, are required to produce 242 grams of magnesium oxide by the reaction

$$2\ Mg + O_2 \longrightarrow 2\ MgO$$

EXERCISE 3-8

In Experiment 7 you determined the number of moles of silver chloride formed in the reaction of some sodium chloride with a known amount of silver nitrate. How many moles of sodium chloride reacted with the silver nitrate? Compare this with the number of moles of sodium chloride you added.

3-7 Review

All chemical reactions are described by the same principles. Whether one is a research chemist investigating new chemical reactions in the laboratory or an engineer involved in the industrial preparation of important chemicals, the same ideas apply. In this chapter we have illustrated these principles.

In any chemical reaction, the bonds between atoms in molecules are broken or new bonds form to give molecular products. *Atoms are conserved in chemical reactions.*

Chemists use balanced chemical equations to describe chemical reactions. Either molecular models or chemical formulas can be used to represent the reactants and products of a chemical reaction. The reactants are placed to the left of an arrow. The products are placed to the right of this arrow. The equation is said to be balanced when the number of each kind of atom is the same on both sides of the arrow.

The balanced chemical equation is the key to the quantitative relationship between the substances that react or form in the chemical reaction. The coefficients in the balanced equation tell us the number of moles of each substance in the reaction. Knowing the number of moles, one can readily calculate the mass of each substance that enters into the chemical reaction.

Questions and Problems for Chapter 3

1

One volume of hydrogen gas combines with one volume of chlorine gas to give two volumes of hydrogen chloride gas. On the basis of many reactions, we have learned that the molecular formulas are H_2 for hydrogen, Cl_2 for chlorine, and HCl for hydrogen chloride. The reaction can be represented with this equation.

$$H_2 + Cl_2 \longrightarrow 2\ HCl$$

- (a) According to this reaction, how many molecules of hydrogen chloride can be formed using one molecule of hydrogen?
- (b) How many moles of hydrogen chloride can be formed using one mole of hydrogen?
- (c) How many molecules of hydrogen chloride can be formed using four molecules of chlorine?
- (d) How many moles of chlorine are required to produce eight moles of hydrogen chloride?

2

The reaction between nitric oxide, NO, and oxygen, O_2, can be written

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

- (a) How many molecules of nitrogen dioxide, NO_2, can be formed using two molecules of nitric oxide?
- (b) How many moles of nitric oxide are needed to give four moles of nitrogen dioxide?
- (c) How many moles of oxygen atoms are there in one mole of oxygen molecules?
- (d) How many moles of oxygen atoms are there in two moles of nitric oxide?
- (e) How many moles of oxygen atoms are there in two moles of nitrogen dioxide?
- (f) Use the answers to parts (c), (d), and (e) to verify that the reaction is written to conserve oxygen atoms.

3

Write the equation for the reaction between nitrogen and hydrogen to give ammonia. The molecular formulas are N_2, H_2, and NH_3 respectively.

- (a) Verify that your equation conserves nitrogen atoms.
- (b) Verify that your equation conserves hydrogen atoms.

4

Balance the equations for each of the following reactions. Begin on the basis of one mole of the underlined substance.

- (a) $Li + \underline{Cl_2} \longrightarrow LiCl$
- (b) $Na + \underline{Cl_2} \longrightarrow NaCl$
- (c) $Na + \underline{F_2} \longrightarrow NaF$
- (d) $\underline{Na} + Br_2 \longrightarrow NaBr$
- (e) $\underline{O_2} + Cl_2 \longrightarrow Cl_2O$
- (f) $O_2 + \underline{Cl_2} \longrightarrow Cl_2O$

Show that your answers to parts (e) and (f) contain the same information.

5

Balance the equations for each of the following reactions involving oxygen. Begin on the basis of one mole of the underlined substance.

- (a) $Ni + \underline{O_2} \longrightarrow NiO$
- (b) $\underline{Ni} + O_2 \longrightarrow NiO$
- (c) $Li + \underline{O_2} \longrightarrow Li_2O$
- (d) With the rocket fuel hydrazine, N_2H_4:

  $$\underline{N_2H_4} + O_2 \longrightarrow N_2 + H_2O$$

- (e) With the important copper ore, chalcocite, Cu_2S:

  $$\underline{Cu_2S} + O_2 \longrightarrow Cu_2O + SO_2$$

- (f) With the important iron ore, iron pyrites, FeS_2. (This ore is sometimes referred to as "fool's gold" because of its bright golden luster.)

  $$FeS_2 + O_2 \longrightarrow \underline{Fe_2O_3} + SO_2$$

6

If 3 grams of substance *A* combine with 4 grams of substance *B* to make 5 grams of substance *C* and some *D*, how many grams of *D* would you expect?

7

When ammonia is decomposed into nitrogen and hydrogen, the reaction absorbs heat energy. The equation can be written this way:

$$2\,NH_3 + 22\,kcal \longrightarrow N_2 + 3\,H_2$$ endo

(a) How many moles of nitrogen will be produced from two moles of ammonia? 1
(b) How much heat energy would be absorbed during the production of one mole of nitrogen? 22
(c) How much heat energy must be absorbed to produce nine moles of hydrogen? 3 × 22 kcal = 66 kCal
(d) Calculate the mass of two moles of ammonia. Compare that number to the sum of the masses of one mole of nitrogen and three moles of hydrogen.

8

Balance the equations for the decomposition of ammonia, nitrogen trifluoride, and nitrogen trichloride into the elements. Base each equation on the formation of one mole of nitrogen.

$$NH_3 \xrightarrow{+22\,kcal} N_2 + H_2$$ endo
$$2\,NF_3 \xrightarrow{+54\,kcal} N_2 + 3\,F_2$$ endo
$$2\,NCl_3 \longrightarrow N_2 + 3\,Cl_2$$ +109 kcal – exo

Rewrite these equations to include this information. Decomposition of ammonia and nitrogen trifluoride are *endothermic* reactions, 22 kcal and 54 kcal per mole of nitrogen, respectively. The decomposition of nitrogen trichloride is *exothermic*, 109 kcal per mole of nitrogen. Which of these three compounds would you expect to be dangerously explosive? rate NCl_3

1st 2 need energy – restricts rate

9

In the manufacture of nitric acid, HNO_3, nitrogen dioxide reacts with water according to this equation:

$$\overset{x=75}{3\,NO_2} + H_2O \longrightarrow 2\,HNO_3 + \overset{25}{NO}$$
6 + 1 = 6 + 1

(a) Verify that the equation conserves oxygen atoms.
(b) How many molecules of nitrogen dioxide are required to form 25 molecules of nitric oxide? 75
(c) How many moles of nitric oxide are formed from 0.60 mole of nitrogen dioxide? .2 mole

3 —— 1
.60 x
∴ 3x = .6
∴ x = $\frac{.6}{3}$ = .2 moles

10

One step in the manufacture of sulfuric acid is the burning of sulfur, S_8, in air to form a colorless gas, SO_2, sulfur dioxide. On the basis of this information:

(a) Write the balanced equation for this reaction.
(b) Interpret the equation in terms of molecules.
(c) Interpret the equation in terms of words.
(d) How many moles of sulfur dioxide can be produced from two moles of sulfur? 16

11

When iron rusts, it combines with oxygen of the air to form iron oxide, Fe_2O_3. Which of the following statements is FALSE?

(a) The equation is $3\,O_2 + 4\,Fe \longrightarrow 2\,Fe_2O_3$ ✓
(b) There are five atoms represented by the formula Fe_2O_3. ✓
(c) Oxygen gas is triatomic. ✗
(d) The mass of the reactants equals the mass of the products. conservation ✓
(e) Atoms are conserved. " ✓

12

Chlorine, Cl_2, is one of the most important industrial chemicals that we know. Each year many tons of chlorine are produced by the electrolysis of sodium chloride. Most of this chlorine is used to purify water supplies or to bleach paper and cloth. The other product of this electrolysis is metallic sodium.

(a) Write a balanced equation for this electrolytic reaction.
(b) How many kilograms of sodium chloride are required to make 1.00×10^3 kilograms of chlorine?

13

Large amounts of the very important metal titanium, Ti, are made by reacting titanium tetrachloride with magnesium metal. Titanium metal and magnesium chloride, $MgCl_2$, are produced.

(a) Write the balanced equation for the reaction.
(b) How many kilograms of magnesium are required to produce one kilogram of titanium?

14

Copper wire reacts with silver nitrate solution to produce silver metal and a solution of copper nitrate, $Cu(NO_3)_2$.

(a) Write a balanced equation for the reaction.
(b) How many grams of metallic silver would be produced if 2.37 g of copper reacted?

15

When iron filings react with a copper sulfate solution, metallic copper and a solution of iron sulfate, $FeSO_4$, are produced.

(a) Write a balanced equation for the reaction.
(b) How many moles of copper would be produced if 2.45 g of iron react with an excess of copper sulfate solution?
(c) How many grams of copper would be produced?

16

Silver reacts with nitric acid as indicated by the equation.

$$Ag + 2\,HNO_3 \longrightarrow NO_2 + AgNO_3 + H_2O$$

(a) How many grams of nitric acid would be required to react with 5.00 g of silver?
(b) How many grams of water would be formed?
(c) How many grams of nitrogen dioxide would be produced?

17

Hydrated copper sulfate, $CuSO_4{\cdot}5\,H_2O$, decomposes, when heated, to form anhydrous copper sulfate, $CuSO_4$, and water.

(a) Write a balanced equation for the reaction.
(b) How many grams of water would form if 5.00 g of the hydrate are heated?
(c) How much of the anhydrous copper sulfate would be produced if 5.00 g of the hydrate is heated?

18

Large amounts of SO_2 needed to make H_2SO_4 are obtained by the reaction shown in Problem 5 (f). The Fe_2O_3 produced is also useful. It can be used in blast furnaces to produce iron (the compound FeS_2 cannot be used in blast furnaces).

(a) How many kilograms of FeS_2 are needed to produce 128 kilograms of SO_2?
(b) Does the Fe_2O_3 weigh more or less than the FeS_2 from which it is made?

19

Use the equation obtained in Problem 10 to answer these questions.

(a) How many kilograms of S_8 are needed to produce 641 kilograms of SO_2?
(b) SO_2 can be burned to form SO_3. How many kilograms of SO_2 are needed to produce 801 kilograms of SO_3?
(c) SO_3 reacts with water to form H_2SO_4. How many kilograms of sulfur are needed to produce 981 kilograms of sulfuric acid?

20

Graphite is one form of carbon, C. It can be burned in air to produce carbon dioxide.

(a) Write the equation for the reaction.
(b) If one mole of graphite is burned, how many moles of carbon dioxide are produced? What is the mass in grams for this amount of carbon dioxide?
(c) If five moles of graphite are burned in a vessel containing 10 moles of oxygen gas, what is the maximum number of moles of carbon dioxide that could be produced?

21

If a piece of sodium metal is lowered into a bottle of chlorine gas, a reaction takes place. Sodium chloride, table salt, is formed.

(a) Write the equation for the reaction.
(b) How many moles of sodium chloride could be formed using one mole of sodium?
(c) How many moles of sodium chloride could be formed using 2.30 grams of sodium?

22

Methane, the principal constituent of natural gas, has the formula CH_4. When it is burned in air, the combustion products are carbon dioxide and water.

(a) Write the equation for the combustion of methane.
(b) How many moles of water could be formed using one mole of methane?
(c) How many moles of water would be produced when 4.0 grams of methane are burned?

23

If potassium chlorate, $KClO_3$, is heated gently, the crystals will melt. When the temperature gets high enough, potassium chlorate decomposes to give oxygen gas and potassium chloride, KCl.

(a) Write the equation for this decomposition.
(b) How many moles of $KClO_3$ are needed to give 1.5 moles of oxygen?
(c) How many moles of KCl would be formed when 0.33 mole of $KClO_3$ decomposes?
(d) How many moles of oxygen would be produced from 122.6 grams of $KClO_3$?

24

One gallon of gasoline can be considered to be about 25 moles of octane, C_8H_{18}.

(a) How many moles of oxygen must be used to burn one gallon of gasoline, forming carbon dioxide and water?
(b) How many moles of carbon dioxide are formed? How many kilograms?
(c) How much carbon dioxide is released into the atmosphere when 10 gallons of gasoline are used in an automobile? Express your answer in pounds as well as kilograms. (1 kilogram = 2.2 pounds.)

25

Iron burns in air to form a black solid oxide, Fe_3O_4.

(a) Write the equation for the reaction.
(b) How many moles of oxygen are needed to react with one mole of iron?
(c) How many grams of oxygen would this be?
(d) Can a piece of iron weighing 5.6 grams burn completely to Fe_3O_4 in a vessel containing 0.05 mole of O_2?

26

The reaction in Problem 9 relates to the manufacture of nitric acid.

(a) How many grams of nitric acid are formed from one mole of nitrogen dioxide, according to the equation in Problem 9?
(b) How many more grams of nitric acid could be made if the nitric oxide, NO, formed could be completely converted to nitric acid?

27

Hydrazine, N_2H_4, can be burned with oxygen to provide energy for rocket propulsion. The energy released is 150 kcal per mole of hydrazine burned.

(a) How much energy is released if 10.0 kg of hydrazine fuel are burned? Look at Problem 5 (d) for the reaction of hydrazine with oxygen.
(b) Compare the energy that would be released if the same mass of hydrogen, 10.0 kg, is burned as fuel instead (see Section 3-1).

28

Although sodium carbonate is needed in the manufacture of glass, very little sodium carbonate is found in nature. It is made using two very abundant chemicals, calcium carbonate (limestone) and sodium chloride. The process involves several steps. The overall reaction can be expressed this way:

$$CaCO_3 + 2\ NaCl \longrightarrow Na_2CO_3 + CaCl_2$$

(a) How many grams of sodium chloride react with 1.00 kg of calcium carbonate?
(b) How many grams of sodium carbonate are produced?

29

A substance used in manufacturing gasoline consists of finely divided platinum supported on an inert solid. Suppose that the platinum is formed by the high temperature reaction between platinum dioxide, PtO_2, and hydrogen gas to form platinum metal and water.

(a) How many grams of hydrogen are needed to produce 1.0 gram of platinum metal?
(b) How many moles of water are produced at the same time? How many grams of water?

30

Hydrazine, N_2H_4, and hydrogen peroxide, H_2O_2, are used together as a rocket fuel. The products of the reaction are nitrogen and water. How many grams of hydrogen peroxide are needed per 1.00×10^3 grams of hydrazine carried by the rocket?

31

The hourly energy requirements of an astronaut can be satisfied by the energy released when 34 grams of sucrose are burned in his body. How many grams of oxygen would need to be carried in a space capsule to meet this requirement? The formula of sucrose is $C_{12}H_{22}O_{11}$. Assume that the products of the reaction are carbon dioxide and water.

The Gas Phase

4

The gaseous state is the simplest state of matter to understand. It is important to chemists because study of gases and their reactions made chemistry a quantitative science. We have already discussed how the regularity in pressure-volume behavior of gases led to the particle model of a gas. This model, in turn, suggested further experiments. We saw how Avogadro interpreted the simple combining ratios of gas volumes in chemical reactions. This interpretation was so very important because it provided an experimental method to measure the molar mass of any gas.

In this chapter we shall explore some additional regularities in gas behavior. These regularities will help us understand the meaning of temperature at the molecular level.

4-1 Pressure-Volume Regularity

In Chapter 1, we found through a simple experiment at constant temperature that the pressure of a gas increases when the gas volume is decreased. This regularity for any gas can be expressed by the equation

$$P \times V = a$$

$$P = \frac{a}{V} \quad \text{or} \quad V = \frac{a}{P}$$

where a is a constant that depends on the temperature and the amount of gas. The equation shows that pressure and volume are inversely related. As one goes up, the other goes down.

Let us carry out the experiment diagrammed in Figure 4-1. Two flasks of the same size are connected through a stopcock which initially is closed. Oxygen gas, at pressure P, is placed in the right-hand flask. The same pressure of nitrogen gas is placed in the left-hand flask. Both flasks are kept at the same temperature throughout this experiment. According to Avogadro's Hypothesis the number of oxygen and nitrogen molecules are equal. Now we are ready to carry out the experiment. It is a very simple one. We open the stopcock and then several hours later we close the stopcock. The manometers

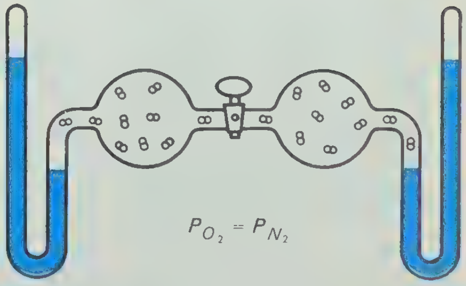


Figure 4-1

Equal pressures of O_2 and N_2.
What happens when the stopcock is opened?

on the flasks show that no pressure change has occurred. Chemical analysis shows that oxygen and nitrogen are present in both flasks. How can we interpret this experiment?

When the stopcock is opened, the volume available to each gas is suddenly doubled. Each gas expands to occupy the two flasks. This spontaneous mixing of two gases is called **diffusion.** The pressure of each gas decreases to one half its original value. The measured gas pressure remains constant throughout the experiment. Initially,

$$P_{\text{measured}} = P_{O_2} = P_{N_2}$$

At the end of the experiment

$$P_{\text{measured}} = p_{O_2} + p_{N_2}$$

where we use the small letter p to indicate the contribution each gas makes to the total pressure. The words **partial pressure of oxygen** are used to describe the symbol p_O. But we also know that

$$p_{O_2} = \tfrac{1}{2} P_{O_2}$$
$$p_{N_2} = \tfrac{1}{2} P_{N_2}$$

because the gas volume was doubled when the stopcock was opened. Substitution of these last values for partial pressure of the two gases shows clearly why the measured pressure did not change during this experiment.

$$\begin{aligned} P_{\text{measured}} &= p_{O_2} + p_{N_2} \\ &= \tfrac{1}{2} P_{O_2} + \tfrac{1}{2} P_{N_2} \\ &= P_{O_2} = P_{N_2} \end{aligned}$$

The total pressure exerted by a mixture of gases is the sum of the individual pressures of the gases.

EXERCISE 4-1

Start with 2 atmospheres pressure of oxygen and 1 atmosphere pressure of nitrogen in the experiment diagrammed in Figure 4-1. What would be the partial pressure of each gas after opening the stopcock? What would the final gas pressure be?

EXERCISE 4-2

Suppose the flask containing O_2 is twice as large as the flask containing N_2. If each gas initially is at one atmosphere pressure, what are the final partial pressures for each gas after the stopcock is opened? What is the final total pressure?

4-2 Volume-Temperature Regularity

Figure 4-2 illustrates an experiment to measure changes in gas volume as the temperature is varied. A drop of mercury traps a sample of air in a long small-bore tube, closed at the bottom. The length of the air sample is a measure of the gas volume. The mercury plug

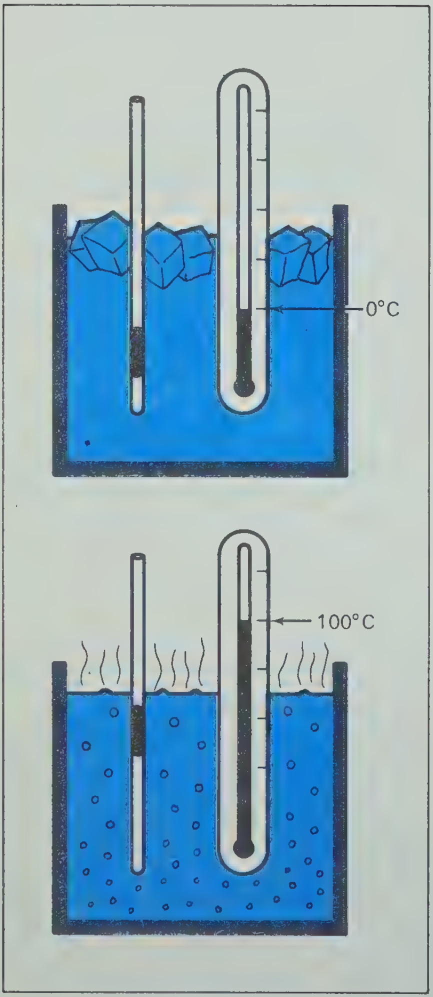


Figure 4-2

Apparatus for demonstrating the effect of temperature *on the volume of a gas.*

moves up or down as the temperature is changed, maintaining constant pressure. The gas volume increases as we increase the temperature. This behavior is another important regularity for gases. All gases behave this way. Careful measurements of the molar volume of NH_3 gas at different temperatures are given in Table 4-1. We would find similar values for one mole of any gas.

TABLE 4-1

Volume of 17.0 grams of NH_3 at 1 atm Pressure

Temperature (°C)	Volume (liters)
−25	20.4
0	22.4
25	24.4
100	30.6
200	38.8

Let's plot this data to see if additional information can be obtained. The straight line in Figure 4-3 illustrates visually the volume-temperature regularity in gas behavior.

The volume of a gas increases as the temperature is increased. The mathematical equation that describes a straight line graph is $y = mx + d$ where m and d are constants for any particular line. For our data we can write the equation

$$V = mt + d$$

$$V = \text{volume in liters}$$

$$t = {}^\circ\text{C}$$

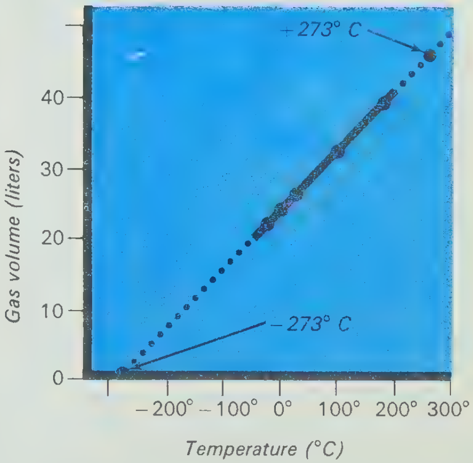


Figure 4-3

Volume *vs* temperature data for one mole of ammonia.

If we extrapolate this line to higher temperatures, we see that the gas volume at 273°C is twice the original gas volume at 0°C. Extrapolation to lower temperatures suggests the surprising result that the gas volume becomes zero at −273°C! When we carry out the experiment of lowering the temperature of a gas more and more, we find that the volume of a gas does not go to zero. Before the temperature gets as low as −273°C, gases liquefy and then change to solids. Nevertheless the straight line relationship between V and t led scientists to wonder if there might not be a lowest possible temperature. This temperature would be really **zero, an absolute zero.** We can simplify the appearance of the equation that describes the volume-temperature relationship. Instead of assigning zero on the temperature scale to the temperature of melting ice (0°C), let us assign zero to the extrapolated temperature (−273°C). This procedure establishes a new temperature scale, called the **absolute scale.** Temperature on this scale is indicated by °K, degrees Kelvin. The size of the degree is the same on the Celsius and Kelvin scales. Only the zero or reference point is different. Temperatures on the two scales are related by the equation

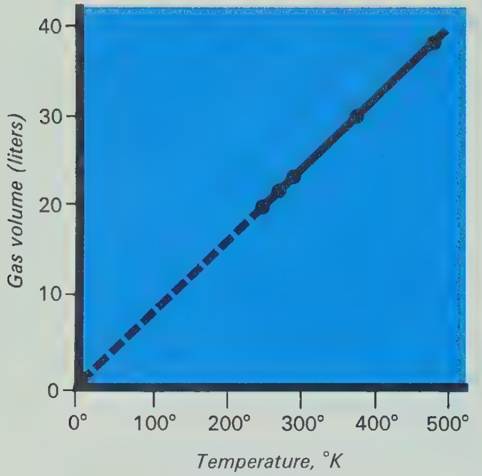


Figure 4-4

Volume vs temperature data for one mole of ammonia.

$T = t + 273°$

T = degrees, on the Kelvin scale

t = degrees, on the Celsius scale

The mathematical equation that describes the straight line seen in Figure 4-4 has the form, $V = bT$, where b is a proportionality constant. The regularity expressed in this equation can be stated in words.

> At constant pressure the volume of a gas is directly proportional to the absolute temperature, T.

EXERCISE 4-3

Express these temperatures in degrees Kelvin:

Water boils at	100°C
Mercury freezes at	−38.9°C
Nitrogen boils at	−196°C
Iron melts at	1535°C

Express these temperatures in degrees Celsius.

Lead melts at	600°K
Room temperature is	298°K
Helium boils at	4°K
Ammonia freezes at	195°K

4-3 Pressure-Temperature Regularity

Let us see what happens to the pressure of a gas as the temperature is changed. The gas volume will be kept constant in this experiment. Once again we will take 17.0 grams of NH_3, one mole. We would find similar pressure values for one mole of any gas.

TABLE 4-2

Pressure for 17.0 grams of NH_3, at a Constant Volume of 22.4 liters

Temperature		Pressure
(°C)	(°K)	(atmospheres)
−25	248	0.91
0	273	1.00
25	298	1.09
100	373	1.37
200	473	1.74

When the volume remains constant, gas pressure increases as the temperature goes up. We might expect this result, for there are many examples in our daily lives. When a kettle of water is heated to boiling, increasing gas pressure lifts the lid, allowing steam to escape. During a long automobile trip, the tires get warm and the air pressure in the tires increases.

The straight line in Figure 4-5 can be expressed mathematically, $P = cT$ where c is a proportionality constant. At constant volume the pressure of a gas is directly proportional to the absolute temperature, T. We have found another important regularity in gas behavior.

The equation also tells us that any factors that affect the pressure of a gas must affect the temperature of a gas. Qualitatively we can see that the mass of a molecule and its velocity should be important in determining the pressure of a gas. After all, a steel ball bearing delivers a bigger "push" in a collision than would the same size glass marble, moving at the same velocity. In addition, a steel ball bearing moving at high velocity exerts a much bigger "push" in a collision than would a slow-moving ball bearing. In the next section we will discuss the way in which temperature is measured. We will then be able to understand how molecular mass and molecular velocity affect the pressure and the temperature of a gas.

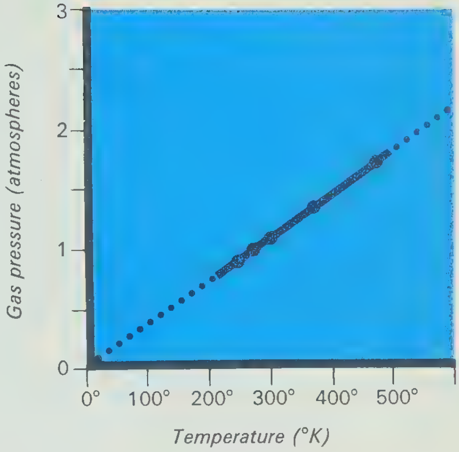


Figure 4-5

Pressure *vs* temperature data for one mole of ammonia.

4-4 The Meaning of Temperature

If someone asked you to measure the temperature of a gas, you would undoubtedly think first of using a thermometer. We can describe what is happening when we use the thermometer. If the thermometer is colder than the gas, heat energy flows into the thermometer until the gas and the thermometer are at the same temperature. We read the scale on the thermometer to know what the gas temperature is. On the other hand, if the thermometer is hotter than the gas, heat energy would flow from the thermometer. When there is no net flow of heat energy, the gas and the thermometer are said to be in **thermal equilibrium.** They are at the same temperature.

There are many kinds of thermometers. Any substance can be used in a thermometer if it has some property that changes with temperature. The thermometer you use in the laboratory depends on the expansion of liquid mercury as the temperature is raised. Gas thermometers are often used in precise scientific measurements. Either a volume change (at constant gas pressure) or a pressure change (at constant gas volume) can serve as the basis for a gas thermometer.

Let us measure the temperature of gas *A* by placing it in thermal contact with a gas *B*, our thermometer. If *A* is initially at a higher temperature than *B*, heat energy flows from *A* to *B*. Our model of a gas helps us to understand what is happening. Molecules of gas *A* have higher energy than the molecules of gas *B*. Molecules of gas *A* collide with the wall separating the two gases. Some of their energy is transferred to molecules of gas *B* on the other side of the wall. It is this transfer of energy which raises the temperature of gas *B*. At the same time the temperature of *A* goes down. It is as though molecules of gas *A* collide *directly* with molecules of gas *B*. The wall only acts to transfer energy. When the two gases are at the same temperature, no further net energy flow takes place. Thermal equilibrium exists.

It is easy to see that we are interested in the molecular motion that carries a molecule up to the container wall. This type of motion is called **translation.** Physicists use the words **kinetic energy** for the energy a particle has because it is moving. (Later in this course we shall see that there are several kinds of molecular motions. At this point we are only interested in translational motion.) The kinetic energy (KE) associated with translation of a particle is related to its mass and to its velocity.

$$KE_{\text{translation}} = {}^1\!/_2\, mv^2$$

When a molecule of gas A is traveling with high velocity, it has high kinetic energy. If it transfers some of its energy through the wall to a molecule of gas B, two things must happen. The kinetic energy of gas B goes up; the kinetic energy of gas A goes down. The temperature of a gas must be directly related to the average translational kinetic energy of the gas. Two gases are at the same temperature when their average translational kinetic energies are equal. We are dealing with one of the most important concepts in science. We can state this concept in words.

Temperature is a measure of molecular translational motion.

or

Molecular translational motion is a measure of **temperature.**

EXERCISE 4-4

At a given temperature, the average KE_{trans} of the molecules in two different gases will be the same. Using NH_3 and HCl as the two gases, explain why NH_3 molecules will have higher velocities than HCl molecules, on the average.

We can see that the Kelvin, or absolute, temperature scale has a new significance because of the relationship between temperature and translational motion. The zero on the absolute scale is the temperature at which there is no longer any translational motion on the molecular level. This temperature is called **absolute zero.** Scientists have discovered methods to reach very low temperatures, within 0.001° of absolute zero.

Substances behave in unusual ways at temperatures near 0°K. Investigations at temperatures within a few degrees of absolute zero form one of the most exciting research areas in science today. It is easy to understand why. Until a substance reaches a very low temperature, the kinetic energy of molecular translation is often so great that it masks the energy effects of some other molecular behavior. Lowering the temperature of a substance minimizes the disturbances caused by molecular translation, making it possible to measure other effects.

4-5 The Kinetic Theory of Gases

The molecules of a gas, even at room temperature, are in rapid motion. They collide with the container walls and with other gas molecules many times each second. At any one instant some molecules experience head-on collisions. Other molecules collide in a glancing manner. We would expect the direction a molecule is moving to change many times each second. In addition, energy is transferred from one molecule to another during a collision. A fast-moving molecule suddenly is slowed down. Then an instant later, after another collision, the molecule may gain energy and move with high velocity again. Because of collisions we would expect gas molecules to travel in all directions and with different velocities.

This description of the nature of a gas is one of the most important theories that scientists have developed. It is based on the particle model. It is essential in the particle model that each particle possesses energy of motion, called kinetic energy. The mathematical expression that describes this model is called the Kinetic Theory of Gases.

4-6 Molecular Velocities

How fast do molecules move? Do all molecules in a sample of gas have the same velocity? At any instant, some molecules will be colliding and others will be moving freely. Probably there is a distribution with some high, some moderate and some low values of velocity. A look at a familiar distribution may be helpful.

There probably are a few students in a typical chemistry class who are very tall. A few of the students are very short. Most students are intermediate in height. Let's count the number of students in each two-inch height interval. Of course, not all the students are the same height. The graph in Figure 4-6 shows that there is quite a range of

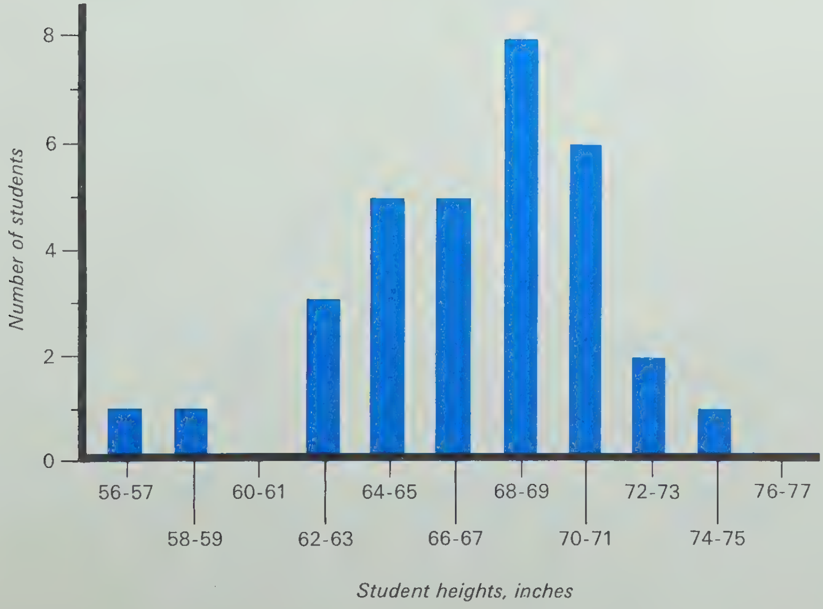


Figure 4-6
Distribution of student heights.

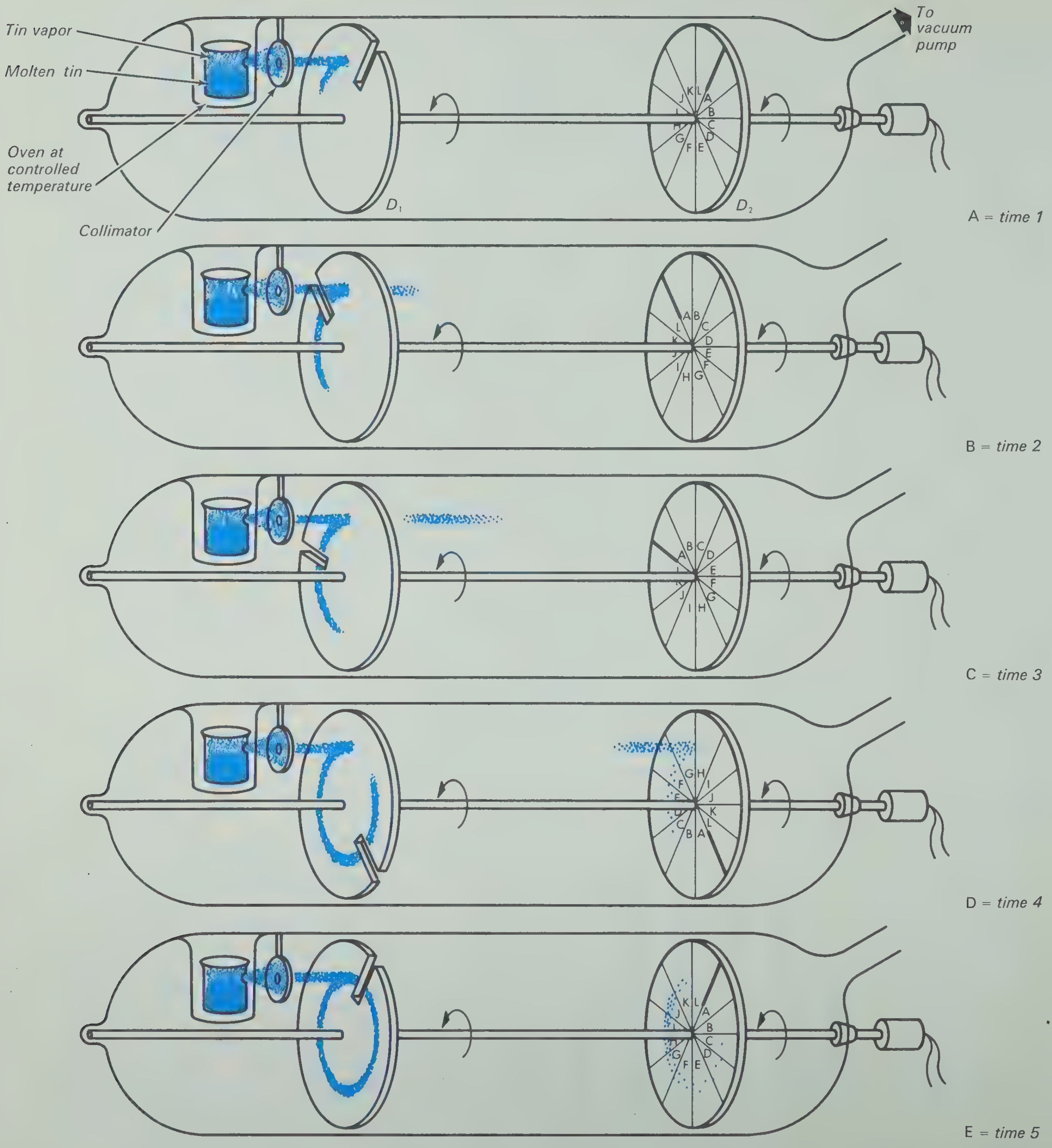

Tin vapor
Molten tin
Oven at controlled temperature
Collimator
To vacuum pump
D_1
D_2
A B C D E F G H I J K L
A = time 1
B = time 2
C = time 3
D = time 4
E = time 5

Figure 4-7

Rotating disc for measurement of molecular velocities.

heights, from 4′8″ to 6′3″. The students in the class are "distributed" over this height range. The bars drawn in this figure indicate the distribution of student heights.

What is the distribution of molecular velocity in a sample of gas? There is an experiment that will provide answers to these questions. The device we use is illustrated in Figure 4-7. Two discs, D_1 and D_2, rotate rapidly on the same axle. These discs are in an evacuated chamber and rotate in front of an oven containing molten tin. Some tin vaporizes and streams out of the small opening in the oven, striking the first rotating disc, D_1. Once during every rotation, the slot in this disc is in line with the hole of the oven. Then a small sample of tin molecules can pass through the slot and move on toward the second disc, D_2. The faster-moving molecules lead the way. Slower-moving molecules begin to lag behind. As the molecules reach the second disc they condense on it. Since this disc also is rotating, fast-moving molecules would condense on sections *B*, *C*, and *D*. Slow-moving molecules take a longer time to reach the second disc. The speed of the rotating discs is adjusted so that the slowest molecules condense on sections *I*, *J*, and *K*. Many different groups of tin molecules pass through the first rotating disc each second. Soon a layer of metallic tin builds up on the second disc. The amount of tin in each of the sections, *A* through *L*, can be determined. The results of such an experiment are shown in Figure 4-8. The largest amount of tin is found on section *I*. In our illustrative experiment, no tin is deposited on the first or last sections, *A* and *L*. From such a disc, the distribution curve shown in Figure 4-9 can be derived.

More information can be extracted from the experiment. We can calculate approximately what velocity a molecule must have to condense on a particular section of disc, D_2. To do this, we must know how far apart the discs are and how fast they rotate. Now we can plot the molecular velocity rather than the section letter on the *x*-axis.

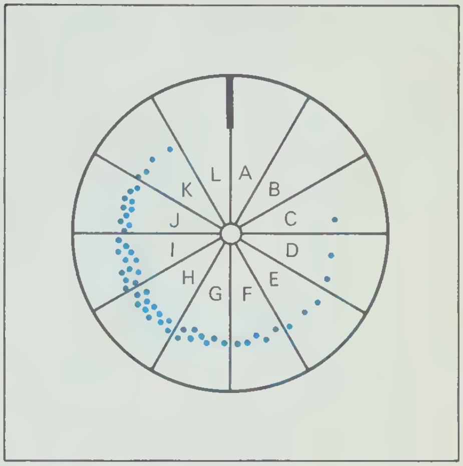


Figure 4-8

Schematic representation of Disc 2 after many revolutions.

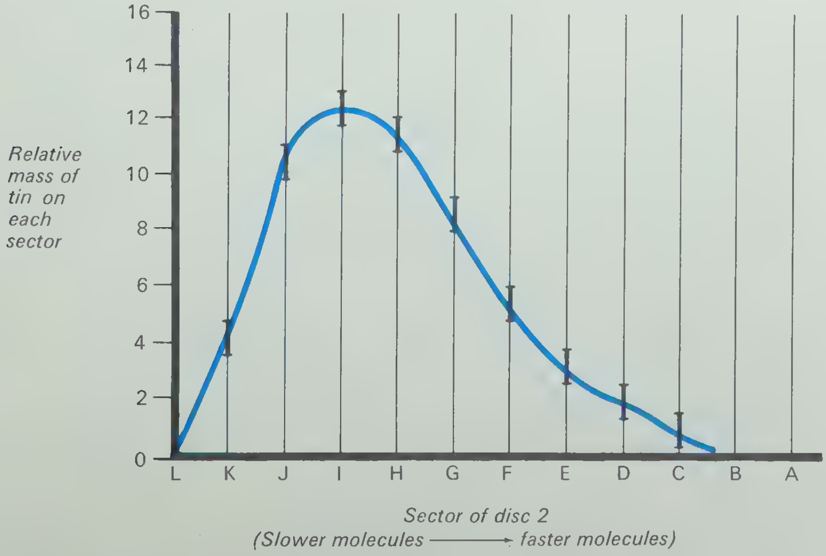


Figure 4-9

Distribution of molecular velocities from rotating disc experiment.

The distribution curve we obtain tells us what fraction of the tin molecules have a particular velocity. A few molecules have very high velocities. A few molecules have very low velocities. Most molecules in a gas have intermediate velocities.

This experiment can be repeated at different temperatures. The results are shown in Figure 4-10 for 500°K and for 1500°K. At the lower temperature the distribution of molecular velocities is rather narrow. Not many molecules have high velocities. As the temperature is increased, more molecules move with high velocity. The distribution curve flattens out. We see that there are always some slow-moving molecules at any temperature. The distribution curves show that there is a smaller fraction of slow-moving molecules at 1500°K than at 500°K. At the same time, the curves show that there is a larger fraction of fast-moving molecules at the higher temperature. From experiments like this, we can get an idea of how fast molecules move. The peaks in the distribution curves tell us that the largest fraction of tin molecules have velocities of about 2×10^4 cm/sec at

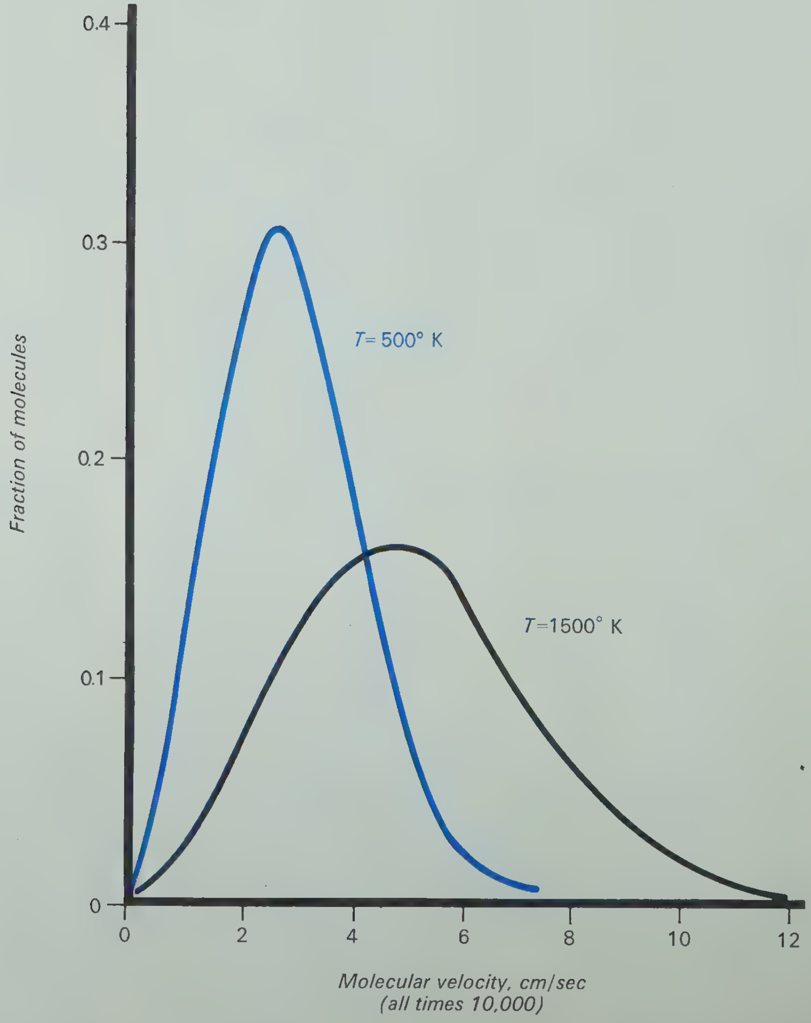


Figure 4-10

Molecular velocity distribution for tin at two temperatures.

fraction of tin molecules have velocities of about 2×10^4 cm/sec at 500°K and about 4×10^4 cm/sec at 1500°K. Table 4-3 gives some numerical values of molecular velocities for different gases and different temperatures. (The average velocity is slightly larger than the peak velocity because the distribution curves are not symmetrical.)

TABLE 4-3

Molecular Velocities

Molecule	Temperature (°K)	Average Velocity (cm/sec)	
H_2	273	18×10^4	(about 1 mile/sec)
H_2	1500	42×10^4	
NH_3	273	7.2×10^4	
O_2	273	4.5×10^4	
Sn	500	3.3×10^4	(about $\frac{1}{6}$ mile/sec)
Sn	1500	5.6×10^4	
Escape Velocity from Earth's Gravitational Field			(about 7 miles/sec)
Jet Airplane at 600 miles/hour			(about $\frac{1}{6}$ mile/sec)

4-7 Molar Volume

We will conclude our treatment of gases by discussing the average distance between molecules. We can get an approximate idea of this distance by comparing the molar volume of ammonia in the solid, liquid, and gaseous states. The molar mass of ammonia, NH_3, is 17.0 grams.

At −79°C, ammonia is a solid with a density of 0.81 gram per cubic centimeter. As the temperature is raised, the solid melts to a liquid at −77°C. Just below the boiling temperature, −33°C, liquid ammonia has a density of 0.68 gram per cubic centimeter. Above the temperature −33°C, ammonia is a gas. Since any gas expands to fill its container, we must indicate both the temperature and the pressure at which we measure its density. We will choose to measure the density of ammonia gas at 0°C and 760 mm pressure. At these conditions, ammonia gas has a density of 7.7×10^{-4} gram per cubic centimeter. This value is much lower than the density of either solid or liquid ammonia. If we divide the molar mass of ammonia by the density, we obtain the volume occupied by one mole of ammonia. If we then divide that number by 6.0×10^{23}, we get an estimate of the volume available to one molecule. See Table 4-4.

TABLE 4-4

Molar and Molecular Volumes of Ammonia

State	Density (g/cm^3)	Molar Volume (cm^3)	Volume per Molecule (cm^3)
Solid	0.81	21	35×10^{-24}
Liquid	0.68	25	41×10^{-24}
Gas (at 0°C, 1 atm)	0.00077	22,400	$37{,}000 \times 10^{-24}$

The volume available to a molecule in a gas is much greater than the volume for a molecule in either the solid or the liquid state. There is about 1000 times more space for the molecule in the gas state. We can understand now why it is easy to compress a gas and why it is very difficult to compress solids or liquids. A gas sample contains a great deal of space between molecules.

EXERCISE 4-5

Explain the experimental observation that diffusion occurs much more rapidly in a gas than in a solid or a liquid.

The numbers in Table 4-4 allow us to make another calculation. It seems reasonable to assume that the volume of a molecule is about the same whether it is in the solid, liquid, or gaseous state. Let us consider that the volume available to a molecule has the shape of a sphere. The formula for the volume of a sphere is $V = {}^4\!/_3\pi r^3$. We can use the numbers in the last column of Table 4-4 to obtain the values of r. The approximate distances between the centers of two molecules are given by $2r$.

Solid $2r = 4 \times 10^{-8}$ cm
Liquid $2r = 4.2 \times 10^{-8}$ cm
Gas $2r = 40 \times 10^{-8}$ cm

These numbers indicate that molecules in a gas are much farther apart than they are in the solid or liquid states.

4-8 Review

We have seen our model for a gas grow as we carried out more experiments. The original suggestion that a gas might be compared with a group of steel ball bearings shaken in a box has proved very useful. Using this model, we can understand the regularities in behavior of a gas.

$$\begin{aligned} PV &= (\text{a constant}) &&= a \\ V &= (\text{a second constant})\ (T) &&= bT \\ P &= (\text{a third constant})\ (T) &&= cT \end{aligned}$$

The model of a gas that we have outlined in our discussion is the basis for one of the most important theories of science, **the Kinetic Theory of Gases.** Let us summarize the nature of a gas. In the next chapter we will see how these ideas can be extended to liquids and solids.

A. A gas is made up of very small particles called *molecules.*
B. Molecules in a gas move with *high average velocities.* There is a range of velocities at any particular tempera-

ture. Some molecules have low velocity. Some molecules have very high velocity.

C. Molecules collide with each other many times each second. We associate the pressure exerted by a gas with the collisions molecules make with the walls of their container.

D. Except at extremely high gas pressure, the volume of the molecules is small compared to the volume of the container.

E. The *absolute temperature* of the gas is a measure of the average kinetic energy of the molecules.

Table 4-5 summarizes some of the numerical values for a typical gas, NH_3.

TABLE 4-5

Properties for One Mole of NH_3 at 0°C and 1 atm Pressure

Molar volume	22,400 cm^3
Number of molecules	6.0×10^{23}
Percentage of empty space	about 99.9%
Volume of one molecule	3.3×10^{-23} cm^3
Average molecular velocity	about 7×10^4 cm/sec
Average distance between two molecules	40×10^{-8} cm
Number of collisions per second for each NH_3 molecule	about 10^9 per second
Average distance traveled between collisions	about 10^{-5} cm

An idea of the distance between molecules in a gas is given by the circles on this page. They represent ammonia molecules (about 4×10^{-8} cm across) separated by approximately 40×10^{-8} cm. Both dimensions are drawn on a scale 25,000,000 times larger than actual.

Questions and Problems for Chapter 4

1

What is the molar mass of a gas if 1.00 liter of the gas weighs 2.00 grams at 0°C and one atmosphere pressure?

2

The gas sulfur dioxide combines with oxygen to form the gas, sulfur trioxide. What value would you expect for each of these ratios?

(a) $\dfrac{\text{number of } SO_3 \text{ molecules produced}}{\text{number of } O_2 \text{ molecules consumed}}$

(b) $\dfrac{\text{volume of } SO_3 \text{ gas produced}}{\text{volume of } O_2 \text{ gas consumed}}$

3

Compressed oxygen gas is sold at a pressure of 130 atmospheres in steel cylinders of 40 liters volume.

(a) How many moles of oxygen are in one of these cylinders?

(b) How many kilograms of oxygen are in one of these cylinders?

4

A 1.50 liter sample of dry air in a cylinder exerts a pressure of 3.00 atmospheres at a temperature of 25°C. Without change in temperature, a piston is moved in the cylinder until the pressure in the cylinder is reduced to 1.00 atmosphere. What is the volume of the gas?

5

Suppose the total pressure in an automobile tire is 30 pounds/inch^2 and we want to increase the pressure to 40 pounds/inch^2. What change in the amount of air in the tire must take place? Assume that the temperature and volume of the tire remain constant.

6

A student collects a volume of hydrogen over water. He determines that there are 2.00×10^{-3} mole of hydrogen and 6.0×10^{-5} mole of water vapor present. If the total pressure inside the collecting tube is 760 mm, what is the partial pressure of each gas?

7

A sample of nitrogen is collected over water at 18.5°C. The vapor pressure of water at 18.5°C is 16 mm. What are the partial pressures of nitrogen and of water if the total pressure is 756 mm?

8

A cylinder contains nitrogen gas and a small amount of liquid water at a temperature of 25°C (the vapor pressure of water at 25°C is 23.8 mm). The total pressure is 600.0 mm. A piston is pushed into the cylinder until the volume is halved. What is the final total pressure?

Answer: 1176 mm.

9

Why does the pressure build up in a tire on a hot day? Answer in terms of the Kinetic Theory.

10

Two glass containers have the same volume. One is filled with hydrogen gas, the other with carbon dioxide gas. Both containers are at the same temperature and pressure.

(a) Compare the number of moles of the two gases.
(b) Compare the number of molecules of the two gases.
(c) Compare the number of grams of the two gases.
(d) The temperature of the container of hydrogen gas is increased. Now compare the pressure, the volume, the number of moles, and the average molecular kinetic energy.

11

Why is it desirable to express all temperatures in degrees Kelvin when working problems dealing with gas relationships?

12

The boiling and freezing temperatures of certain liquids are listed below. Express these temperatures on the absolute temperature scale.

Liquid helium	boiling temperature	−269°C
Liquid hydrogen	freezing temperature	−259°C
Liquid hydrogen	boiling temperature	−253°C
Liquid nitrogen	freezing temperature	−210°C
Liquid nitrogen	boiling temperature	−196°C
Liquid oxygen	freezing temperature	−219°C
Liquid oxygen	boiling temperature	−183°C

13

How many molecules are there in a molar volume of a gas at 100°C? at 0°C?

14

If 1.00×10^2 ml of a gas at 10°C are heated to 20°C, the volume of the gas will be approximately: (Pressure and number of molecules are kept constant.)

(a) 50 ml
(b) 100 ml
(c) 103 ml
(d) 200 ml
(e) 375 ml

15

What is the molar volume of water under each of the following conditions?

(a) Solid, 0°C. Density of ice = 0.915 g/ml
(b) Liquid, 0°C. Density of water = 1.00 g/ml
(c) Gas, 100°C. Density of water vapor (100°C and 1 atm) = 5.88×10^{-4} g/ml

16

Compare your answers in Problem 15 with the values for ammonia given on page 65. You know that an ice cube floats in water. Would an ammonia "ice cube" float or sink in liquid ammonia?

17

A carbon dioxide fire extinguisher of 3 liters volume contains 4.4 kilograms of CO_2. What volume of gas could this extinguisher deliver at 25°C and one atm pressure?

18

Hydrogen for weather balloons is often supplied by the reaction between solid calcium hydride, CaH_2, and water to form solid calcium hydroxide, $Ca(OH)_2$, and hydrogen gas.

(a) Balance the equation for the reaction between water and calcium hydride.
(b) How many moles of CaH_2 would be required to fill a weather balloon with 250 liters of hydrogen at 25°C and one atm pressure?
(c) What mass of water would be required to generate the hydrogen?

19

A gas phase reaction between methane, CH_4, and oxygen, O_2, is carried out in a sealed container. Under the conditions used, the products are carbon dioxide and hydrogen. The reaction is exothermic so the temperature rises during the reaction.

(a) Will the final pressure be greater or less than the original pressure?
(b) By what factor does the pressure change if one mole of methane and one mole of oxygen react (the temperature changes from 25°C to 200°C)? *Answer:* 2.38.

20

Combustion of gasoline, typical formula C_8H_{18}, provides the energy to propel an automobile. As the gasoline burns in the car cylinder, the pressure increases and forces the piston down. This motion in turn is transmitted to the wheels of the car. Oxygen reacts with the gasoline to form carbon dioxide and water, releasing enough energy to heat the gas from 300°K to about 1500°K.

(a) Balance the equation for the reaction.
(b) Decide whether the work done by the gas in the cylinder is mainly the result of pressure rise caused by the change in number of moles of gas or the result of pressure rise from heating.

21

A vessel contains equal numbers of oxygen and hydrogen molecules. The pressure is 760 mm when the volume is 50 liters. Which of these statements is FALSE?

(a) On the average, the hydrogen molecules are traveling faster than the oxygen molecules.
(b) On the average, more hydrogen molecules strike the walls per second than oxygen molecules.
(c) If the oxygen were removed from the system, the pressure would drop to 190 mm.
(d) Equal numbers of moles of each gas are present.
(e) The average kinetic energies of oxygen and hydrogen molecules are the same.

22

The vapor pressure of a molten metal can be measured with a device called a Knudsen cell. This is a container closed across the top by a thin foil pierced by a small hole of known diameter. The cell is heated in a vacuum until the vapor streams from the small hole (it *effuses*). The mass of the material escaping per second tells the rate at which gaseous atoms leave. Two identical Knudsen cells are heated at 1000°C. One cell contains lead and the other cell contains magnesium.

(a) Contrast the average kinetic energies of the lead and magnesium atoms within each cell.
(b) Contrast the average velocities of the lead and magnesium atoms leaving each cell.
(c) At a fixed temperature, the rate at which atoms leave the cell is determined by two factors, the vapor pressure and the mass of the gaseous atoms. Explain.

23

The boiling temperatures and the molar volumes at STP of some common gases are listed in the following table.

(a) What regularity is suggested in the relationship between the boiling temperatures and molar volumes?
(b) Account for this regularity.

Gas	Molecular Formula	Boiling Temperature (°C)	Molar Volume (liters)
helium	He	−269	22.426
nitrogen	N_2	−196	22.402
carbon monoxide	CO	−190	22.402
oxygen	O_2	−183	22.393
methane	CH_4	−161	22.360
hydrogen chloride	HCl	−84.0	22.248
ammonia	NH_3	−33.3	22.094
chlorine	Cl_2	−34.6	22.063
sulfur dioxide	SO_2	−10.0	21.888

24

A reaction involved in the production of iron from iron ore is

$$Fe_2O_3 + CO \text{ gives } Fe + CO_2$$

(a) How many kilograms of CO are needed to produce 1.0 kg of Fe?

(b) How many liters of CO (at STP) are needed to produce 1.0 kg of Fe?

25

A compound found in kerosene, a mixture of hydrocarbons, is decane, $C_{10}H_{22}$. A stove might burn 1.0 kg of kerosene per hour. Assume kerosene is decane.

(a) How many liters of oxygen at STP are needed per hour?

(b) How many liters of carbon dioxide at STP are produced per hour?

26

How many grams of zinc metal are needed to react with hydrochloric acid to produce enough hydrogen gas to fill an 11.2 liter balloon at STP? What would the volume of this balloon be at 27°C and 680 mm pressure? How many grams of zinc would be required if sulfuric acid were used instead of hydrochloric acid?

27

How many liters of air at STP are needed to burn 2.2 liters of methane, also at STP? Assume air is 20% oxygen by volume.

28

In the reaction $NH_3 + O_2$ gives $NO + H_2O$; how many liters of oxygen are required to react with 4.48 liters of ammonia? All gases are measured at STP.

29

The following reaction is carried out with all gas volumes measured at the same temperature and pressure.

$$C_4H_{10} + O_2 \text{ gives } CO_2 + H_2O$$

(a) How many liters of oxygen are required to produce 2.0 liters of CO_2?

(b) If 15 liters of oxygen are used, how many liters of butane, C_4H_{10}, will be burned?

(c) If 8.0 liters each of oxygen and butane are mixed, how many liters of CO_2 are produced?

30

What volume of Cl_2 gas at 37°C and 753 mm pressure could be obtained from 58.4 liters of HCl, measured at the same temperature and pressure, if the following reaction takes place?

$$HCl + O_2 \text{ gives } H_2O + Cl_2$$

31

Suppose 105 liters of NH_3 and 285 liters of O_2 are allowed to react until this reaction is complete.

$$NH_3 + O_2 \text{ gives } H_2O + NO_2$$

All volume measurements are made at 200°C and 0.30 atm pressure. Which gas, ammonia or oxygen, remains at the end of the reaction? How many moles of it would there be?

Liquids and Solids An Extension of the Kinetic Theory

5

Only a few substances are gases at normal temperatures and pressures. Almost all of the substances that chemists have prepared are liquids and solids. In this chapter we will apply the Kinetic Theory to liquids and solids.

In the last chapter we proposed that the molecules in liquids and solids are very close together while molecules in a gas are relatively far apart. Remember that one mole of water, 6.0×10^{23} molecules, occupies about 18 milliliters as a liquid. The same number of molecules for a gas at STP would occupy a volume about a thousand times greater. Substances having very strong forces between molecules are solids at room temperature. Substances with weak forces between molecules are gases at room temperature. The average kinetic energy of gas molecules is large enough to overcome the attractive forces between molecules. As the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually the attractive forces between molecules become important relative to the kinetic energy of the molecules. The gas condenses to a liquid. Formation of dew on the grass or condensation of steam are familiar examples of the **phase change,** gas to liquid. In liquids, molecules are close to each other. However, they still have enough energy to move in a random fashion in the liquid phase. When the temperature of a liquid is lowered still further, the average kinetic energy decreases further. The attraction between molecules increases and soon becomes so much greater than the kinetic energy that the liquid changes to a solid. The molecules in the solid take up the regular positions characteristic of a crystalline solid. Water freezing to ice is an example of the phase change, liquid to solid. Ice melting to water is the reverse phase change, solid to liquid.

Phase changes are often referred to as **physical changes.** Chemists are interested in phase changes for a number of reasons. If a substance can be vaporized, measurement of the gas volume provides a way to calculate the molar mass for the substance. The melting temperature of a substance often helps the chemist identify it or estimate its purity. Phase changes serve as relatively simple methods to separate one substance from another.

In this chapter phase changes of pure substances will be discussed. We have already seen qualitatively how a comparison of the attraction between molecules and the average kinetic energy is important in understanding the temperature at which phase changes occur. Potential energy is important too. Let us see what scientists mean when they use the term potential energy.

5-1 Potential Energy

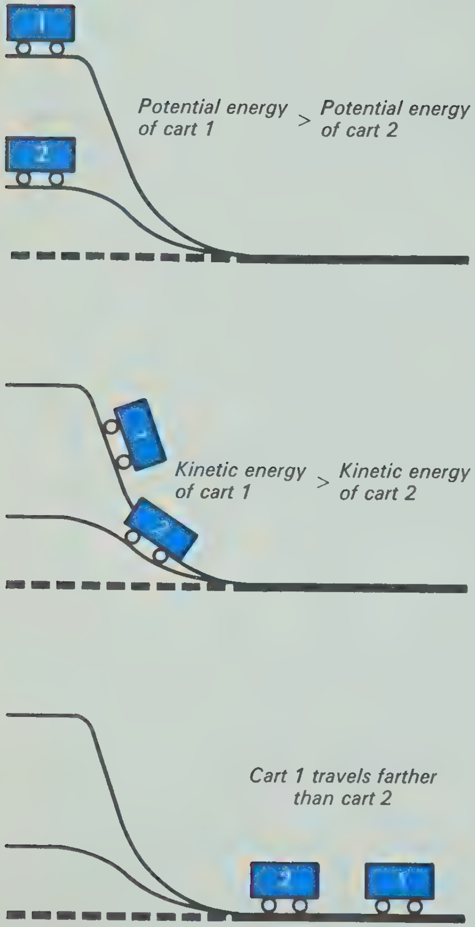

1
2
Potential energy of cart 1 > Potential energy of cart 2
1
2
Kinetic energy of cart 1 > Kinetic energy of cart 2
Cart 1 travels farther than cart 2
2
1

Figure 5-1

Transformation of potential energy into kinetic energy.

Which has more energy, a brick one foot up in the air or the same brick six feet up? If you drop each one on your foot, the answer would be all too obvious! Let us do a more careful experiment than that. Suppose we had two carts at the tops of the two hills shown in Figure 5-1. When we move the carts over the edge of the plateau, they start to roll downhill. The carts gain kinetic energy. As you can tell from the illustration, cart 1 will acquire more kinetic energy than cart 2. Cart 1 moves faster and rolls farther than cart 2. But where does this energy come from?

Work must be done at the start of the experiment to raise the two carts to the tops of the hills. Energy is needed to do that work. Apparently this energy is "stored" in the carts until we let them roll back downhill. The energy is released as the carts move. The term **potential energy** is used to describe energy stored up in this fashion.

Another experiment will help us understand potential energy. Suppose that we push the cart shown in Figure 5-2. The cart moves with constant speed towards a spring which is firmly attached to a very thick wall. The problem is simplified if we make two assumptions. First, there is no friction on this table and second, the wall is so massive that it does not move during the experiment. The cart moves in a straight line until it hits the spring. The cart slows down rapidly as the spring is compressed. For an instant there is no motion in the cart or the spring. Then everything reverses. The spring uncoils. The cart rebounds in the opposite direction regaining its original speed.

Look only at the cart for a minute. It starts with a certain amount of kinetic energy. This energy disappears as the cart compresses the spring and comes to a stop. Then the cart gains back its original kinetic energy as it moves in the opposite direction. What can we say about energy changes in this experiment? Initially the kinetic energy of the moving cart is some constant quantity, *A*. During the collision with the spring, the cart rapidly slows down. The kinetic energy of the cart decreases from *A* to *a* to *zero* at the moment the spring is compressed its maximum amount. Then everything operates in reverse. The spring begins to uncoil; the cart moves in the opposite direction. The kinetic energy of the cart changes from *zero* to *a*, and then to *A*, its original kinetic energy. Scientists say that the original kinetic energy is stored as potential energy in the coiled spring. Energy is being transformed from one type of energy to another.

Figure 5-2 illustrates what happens at different times during the collision. We can represent the energy changes in this manner:

	KINETIC ENERGY OF CART	+	POTENTIAL ENERGY OF SPRING*	=	TOTAL ENERGY OF SYSTEM
Initial constant speed	A	+	0	=	A
Cart slowing down	a	+	b	=	A
No motion	0	+	A	=	A
Cart speeding up	a	+	b	=	A
Final constant speed	A	+	0	=	A

The cart striking the spring is similar to a molecule rebounding from a wall. As long as the wall does not move, the molecule rebounds with its original kinetic energy. We will encounter both kinetic energy and potential energy many times in this course. In what way does potential energy help us understand phase changes?

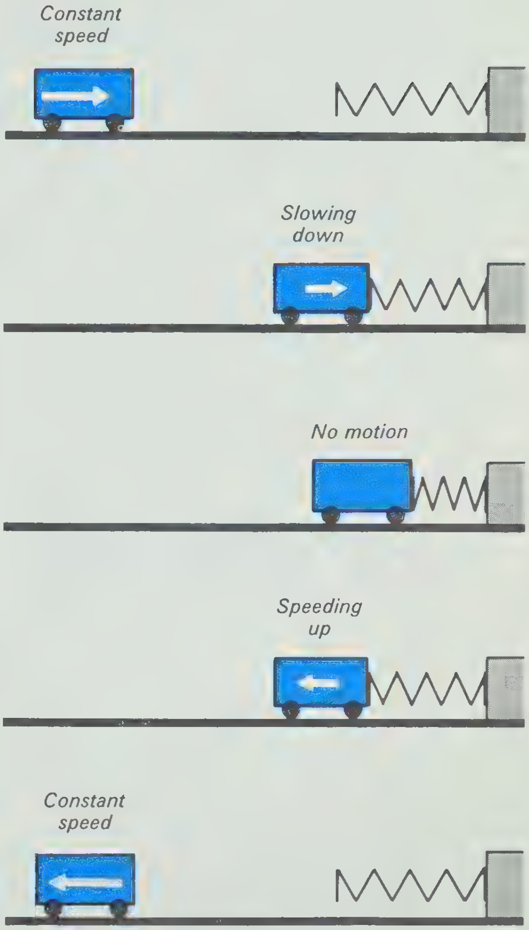


Figure 5-2

Transformation of energy in an elastic collision.

5-2 Solid-Liquid Phase Changes

Solids and liquids are called **condensed phases.** The attractive forces in a condensed phase tend to hold molecules close together. What happens when we add energy to a solid?

When the molecules in a solid are arranged in an orderly repeating pattern, we use the word **crystalline** to describe the solid. At any temperature there is always some molecular motion in a crystal. The molecules move, to a slight extent, back and forth about their positions in the crystal. As energy is added to a solid, the temperature and the motion increase. When the temperature gets high enough, the molecular motion disturbs the regular crystal pattern more and more. Too much of this movement destroys the crystal structure completely. The solid melts, with no change in temperature.

$$H_2O(\text{solid}) + \text{energy} \longrightarrow H_2O(\text{liquid})$$

or more simply

$$H_2O(s) + \text{energy} \longrightarrow H_2O(l)$$

In Experiment 12 you determined the melting curve for *para*-dichlorobenzene. Similar diagrams would be found for other pure solids. The melting curve for water is shown in Figure 5-3. We can see that something unusual is happening during the melting of the solid phase. We continue to add energy to the system. However, once the liquid phase appears, the temperature stays constant until

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* We neglect the very small kinetic energy of the spring as it is compressed or extended.

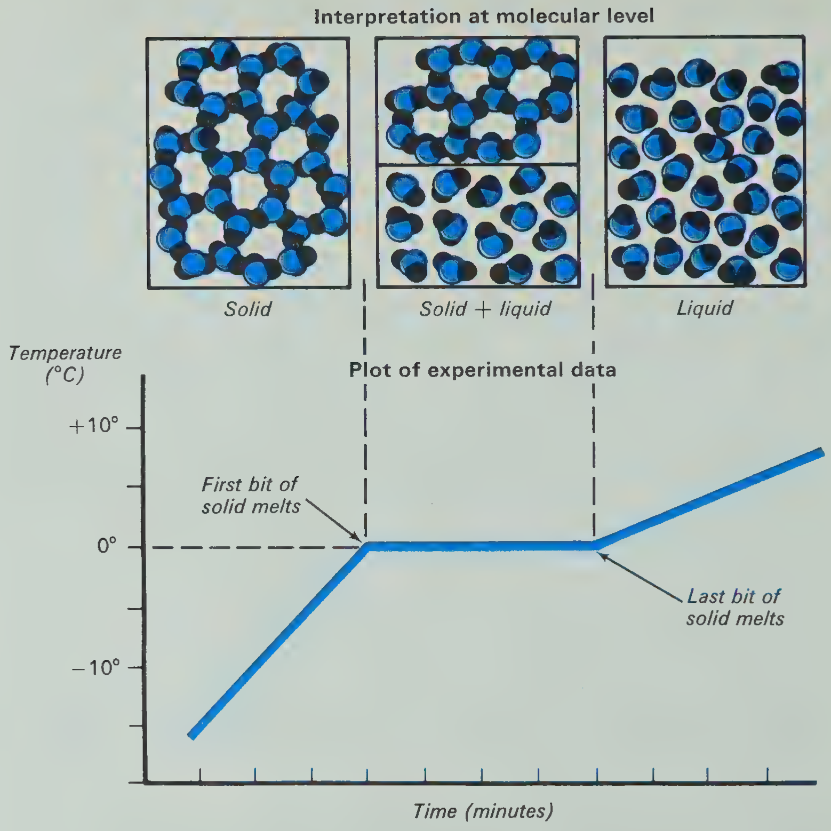


Figure 5-3

Phase change $H_2O(s) \longrightarrow H_2O(l)$. Heat energy is being added slowly at a constant rate.

all of the solid has changed to liquid. This temperature is called the **melting temperature** of the solid.

Where does the energy go this time? During the melting process, the temperature of the liquid phase is the same as the temperature of the solid phase. The energy we supply is not increasing the temperature of either phase. This energy destroys the crystal lattice and is stored in the liquid phase as potential energy.

We can indicate in the equation the amount of energy required to melt one mole of ice at 0°C.

$$H_2O(s) + 1.44\text{ kcal} \longrightarrow H_2O(l)$$

This amount of energy is called the **molar heat of melting** or the **molar heat of fusion.** This is the energy required to overcome the forces that hold 6.0×10^{23} molecules in their regular positions in the crystal.

When we look at the different substances in Table 5-1, we find a range of energy values for molar heats of melting. The molar heats of melting in these examples vary from 0.080 kcal/mole for neon to 6.8 kcal/mole for sodium chloride, a change by a factor of 85. There are very great differences in the forces that bind these solids. Since these differences affect properties other than melting temperature and heat of melting, they are important to a chemist.

TABLE 5-1

The Temperature and Heat of Melting for Some Pure Substances

	Melting Temperature		Molar Heat of Melting
Substance	°K	°C	(kcal/mole)
Neon, Ne	24.6	−248.4	0.080
Chlorine, Cl_2	172	−101	1.53
Water, H_2O	273	0	1.44
Sodium, Na	371	98	0.63
Sodium chloride, NaCl	1081	808	6.8
Copper, Cu	1356	1083	3.11

5-3 Liquid-Gas Phase Change

We can continue to add energy to our sample of liquid water. The temperature rises. Molecules in the liquid acquire higher kinetic energy. Soon the water boils. The temperature stays constant as long as liquid water remains. We call this temperature the boiling temperature of the liquid.

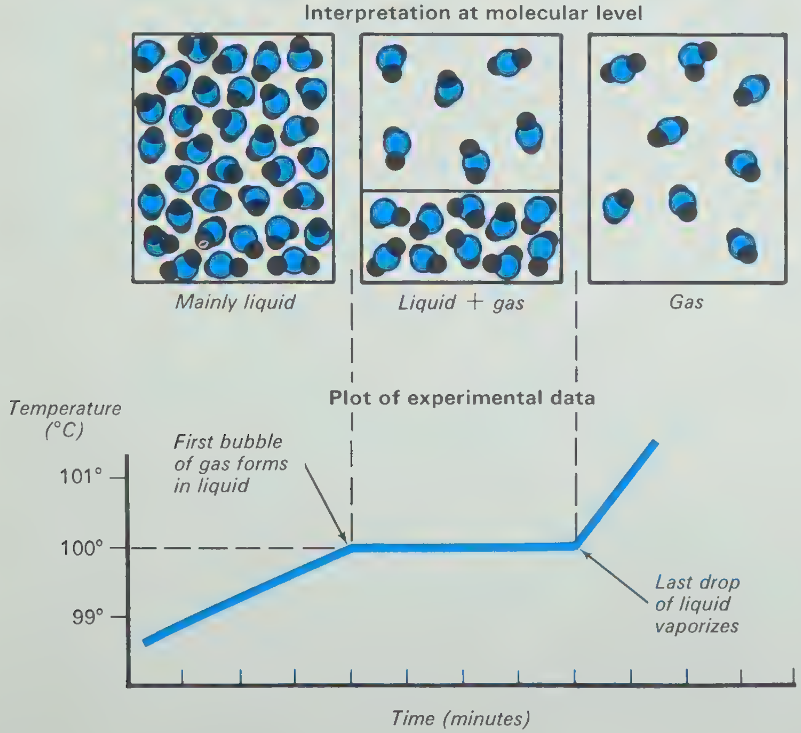


Figure 5-4

Phase change $H_2O(l) \longrightarrow H_2O(g)$. Heat energy is being added slowly at a constant rate.

$$H_2O(\text{liquid}) + \text{energy} \longrightarrow H_2O(\text{gas})$$

or

$$H_2O(l) + \text{energy} \longrightarrow H_2O(g)$$

We can see in Figure 5-4 that addition of energy at 100°C does not increase the temperature in our system as long as both liquid and vapor are present. The average kinetic energy for molecules in the vapor phase at 100°C equals the average kinetic energy for molecules in the liquid phase at 100°C. How do we know? Because the two phases are at the same temperature. The energy to vaporize a liquid must be stored as potential energy in the vapor. This energy overcomes attractive forces in the liquid. Molecules can store energy by being far apart. For water at 100°C the **molar heat of vaporization** is 9.7 kilocalories.

$$H_2O(l) + 9.7\ \text{kcal} \longrightarrow H_2O(g)$$

When water vapor condenses to liquid water, the potential energy is released in the form of heat energy.

$$H_2O(g) \longrightarrow H_2O(l) + 9.7\ \text{kcal}$$

This phase change takes place when raindrops form. Just think of the energy that is released during a severe rainstorm!

EXERCISE 5-1

Calculate approximately how much energy is released when there is 1 cm of rain over an area of 10^{11} cm^2 (about 100 square miles). The density of water is 1 g/cm^3.

Answer. 5.4×10^{10} kcal.

The boiling temperature and heat of vaporization for various liquids are given in Table 5-2. In each example energy is absorbed as the liquid vaporizes.

TABLE 5-2

The Normal Boiling Temperature and Heat of Vaporization of Some Pure Substances

Substance	Boiling Temperature °K	°C	Molar Heat of Vaporization (kcal/mole)
Neon, Ne	27.2	−245.8	0.405
Chlorine, Cl_2	238.9	−34.1	4.88
Water, H_2O	373	100	9.7
Sodium, Na	1162	889	24.1
Sodium chloride, NaCl	1738	1465	40.8
Copper, Cu	2855	2582	72.8

5-4 Vapor Pressure in Liquid-Vapor Equilibrium

The Kinetic Theory helps us to understand the vaporization of a liquid at its boiling temperature. But liquids vaporize at all temperatures.

Let us consider this behavior, beginning with liquid water again. If we place liquid water in an evacuated flask at 25°C and close off the flask, we can measure the gas pressure with a manometer. The gas pressure rises rapidly from 0 mm to 23.8 mm. Then no further pressure change occurs as long as the temperature is kept at 25°C. How can we interpret this experiment?

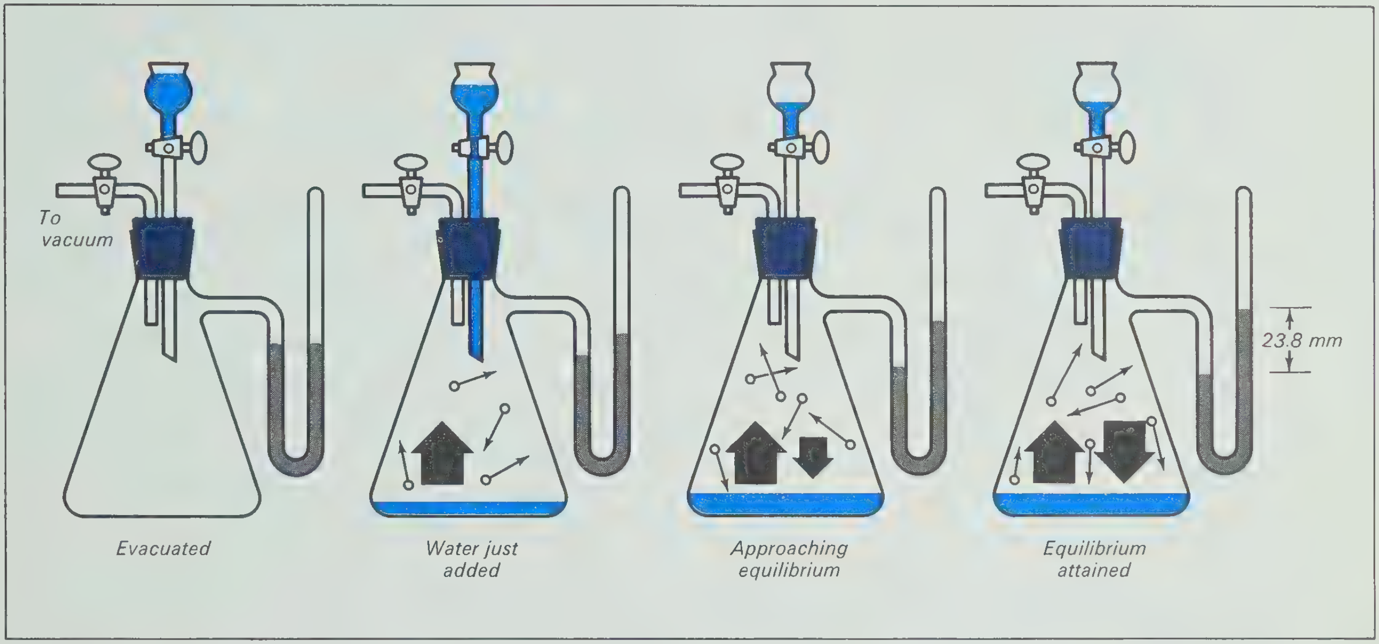


Figure 5-5

Equilibrium between liquid and vapor. Water at 25°C.

Water is the only substance in our system. Some water molecules must leave the liquid phase and enter the vapor phase to account for the gas pressure. This explanation seems quite reasonable. Our model of a liquid pictures molecules moving in a random fashion, with a range of velocities. Some molecules, near the surface of the liquid, would have enough energy to move out of the liquid into the vapor phase. As the number of molecules in the vapor phase increases, the gas pressure rises. After a while the gas pressure reaches a constant value, 23.8 mm. Does this mean that water molecules no longer leave the liquid? This suggestion does not seem very reasonable. After all, there still are many molecules in the liquid moving with high velocities. If we look at the vapor phase, we know that the gas molecules are also moving in a random fashion, with a range of velocities. Every once in a while, a gas molecule would return to the liquid. We can understand now why the gas pressure becomes constant. Molecules leave the liquid phase to enter the vapor. At the same time molecules leave the vapor phase to become part of the liquid again. Figure 5-6 shows what is happening. At first there are many more molecules leaving the liquid each second than returning. After a very short time, the gas pressure goes up. The number of molecules in the vapor phase increases. The chance that a molecule will move back into the liquid phase also increases. Soon the two processes balance each other. The pressure stays constant. This pressure is called the **vapor pressure of water.** It remains at 23.8 mm as long as the temperature is kept at 25°C.

EXERCISE 5-2

Suppose one mole of water evaporates in one day. Approximately how many molecules leave the liquid each second?

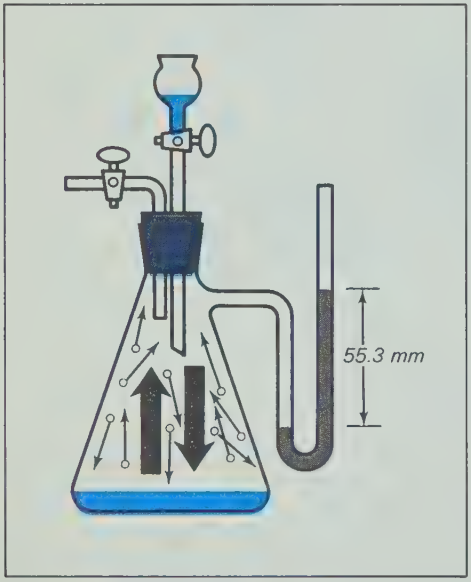


Figure 5-6

The equilibrium vapor pressure for water at 40°C.

The vapor pressure of a liquid is the same whether or not other gases are present. It is a property of the liquid. In our experiment, if the flask originally contained dry air at a pressure of 750.0 mm, liquid would evaporate until the pressure became 773.8 mm.

> When a liquid is in contact with a constant pressure of its vapor, the liquid and gas are said to be in **equilibrium.**
>
> At equilibrium, no measurable changes are taking place.

5-5 Change of Vapor Pressure with Temperature

The vapor pressure of water at 25°C is 23.8 mm. At 40°C, the vapor pressure is 55.3 as shown in Figure 5-6. At 60°C, it is 149.4 mm and at 100°C, it is 760 mm. The vapor pressure of water increases with increasing temperature.

Ethyl alcohol is also a liquid at room temperature. Its vapor pressure at 25°C is 59 mm. This value is higher than the vapor pressure of water at this temperature. Ethyl alcohol has a greater tendency than water to evaporate. At 40°C, ethyl alcohol has a vapor pressure of 135 mm. At 60°C the vapor pressure is 353 mm. We find that the vapor pressure of ethyl alcohol also increases rapidly with increasing temperature. *The vapor pressure of every liquid increases as the temperature is raised.*

These results can be readily explained in terms of the Kinetic Theory. As the temperature increases, the average molecular velocity increases. We would expect that the fraction of molecules in the liquid with sufficient energy to enter the vapor phase would increase at higher temperatures.

Molecules can escape from the surface of a liquid at any temperature to enter the gas phase as vapor. When the vapor pressure of the liquid just equals the atmospheric pressure, a new phenomenon occurs. At this temperature bubbles of vapor can form in the liquid. The liquid boils. We see that boiling is fixed by the external pressure. For example, if the pressure is 760 mm, water boils at 100°C. This is the temperature at which the vapor pressure of water equals 760 mm. Figure 5-7 shows a bubble forming in water at 100°C. The vapor pressure inside the bubble is equal to 760 mm, balancing the external atmospheric pressure. Suppose that the atmospheric pressure is 750 mm. Then bubbles of vapor could form throughout the liquid water at 99.6°C. The vapor pressure of water equals 750 mm at 99.6°C. Water boils at this temperature when the atmospheric pressure is 750 mm.

The normal **boiling temperature** of a liquid is *the temperature at which the vapor pressure of that liquid is exactly one standard atmosphere, 760 mm Hg.*

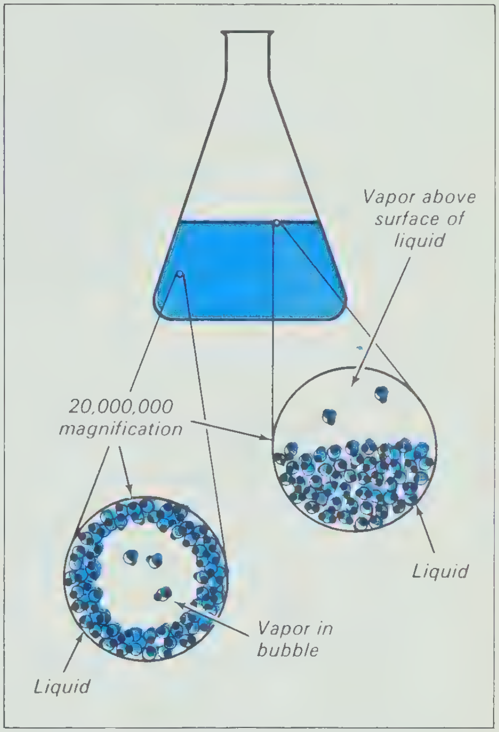


Figure 5-7
Formation of a bubble of water vapor at 100°C.

EXERCISE 5-3

Compare the data for the vapor pressure of water and ethyl alcohol to estimate the boiling temperature of ethyl alcohol.

5-6 Vapor Pressure in Solid-Vapor Equilibrium

Solid carbon dioxide is often called "Dry Ice." At normal pressures, Dry Ice evaporates without melting. The process of a solid going directly to the vapor without forming a liquid first is called **sublimation.** Another example of sublimation can be seen if you live in an area where the winters are very cold. Some snow disappears without the temperature ever rising to 0°C.

Let us do an experiment to see if we can understand what might be happening. If we place some ice in an evacuated flask and keep the temperature below 0°C, no liquid water forms. However, the gas pressure in the flask increases. If we keep the temperature at −10°C, the pressure reaches 2.15 mm. Some water molecules leave the crystal surface and enter the gas phase. The vapor pressure for ice at −10°C is 2.15 mm. Now let us increase the temperature to −5°C. We should expect more water molecules would have enough energy to leave the solid. The equilibrium vapor pressure should go up. We find the vapor pressure for ice at −5°C is 3.16 mm.

The Kinetic Theory provides an explanation for the vapor pressure of a liquid or a solid.

5-7 Review

In this chapter we have seen how the Kinetic Theory can be applied to condensed phases as well as to gases. The magnitude of the forces acting between molecules determines whether a substance is a solid, liquid, or gas at a particular temperature. The forces between molecules must be weak for a substance that is a gas at room temperature and very strong in solids with high melting temperatures.

During any phase change, the temperature stays constant. An understanding of the terms potential energy and kinetic energy lets us interpret phase changes at the molecular level.

In a closed system at constant temperature, some molecules of a liquid or solid have enough energy to move into the vapor phase. At equilibrium there is a balance between the number of molecules entering the vapor phase and the number of molecules returning to the condensed phase.

The normal *boiling temperature* of a liquid is the temperature at which the vapor pressure of that liquid is equal to one standard atmosphere, 760 mm.

Questions and Problems for Chapter 5

1

When a ball is thrown straight up, at what point or points in its trajectory does it have

(a) maximum potential energy?
(b) maximum kinetic energy?
(c) minimum potential energy?
(d) minimum kinetic energy?

2

Discuss the potential and kinetic energy that a skier has

(a) as he gets aboard the ski lift.
(b) as he travels to the top of the ski slope.
(c) as he skis down the hill and reaches the bottom of the ski slope.

3

Discuss the various kinds of energy involved when you ride an elevator to the tenth floor of an office building.

4

A dam, such as the Hoover Dam on the Colorado River, stores water. It also can be said to store energy. Explain.

5

How much heat energy must be removed to freeze an ice tray full of water at 0°C if the ice tray holds 540 grams of water? What happens to this heat energy?

6

Compare the potential energy of 10 grams of solid water and 10 grams of liquid water, both samples at 0°C.

7

A metal cylinder, initially at 25°C, is placed in an insulated cup containing water and crushed ice. After the system has come to thermal equilibrium, there is ice remaining.

(a) What is the equilibrium temperature of the metal cylinder?
(b) What happens to the energy given up by the metal cylinder?
(c) If 20 grams of ice were melted, how much energy was given up by the cylinder?

8

When the temperature drops below 0°C, the fruit on the trees in an orchard can sometimes be protected by flooding the orchard. Why?

9

In an experiment, 100 grams of water at 80°C is allowed to interact with ice (at 0°C). Enough ice is used to cool the water to 0°C. The ice and water are placed in an insulated container so that all the energy given up by the water melts ice. After the system reaches equilibrium at 0°C, there are 200 grams of liquid water present.

(a) How much ice is melted?
(b) How much energy is given up by the 100 grams of water in cooling from 80°C to 0°C?
(c) How much energy is required to melt 1.0 gram of ice?
(d) How much energy is required to melt 1.0 mole of ice?

10

What amount of ice must be added to 540 grams of water at 25°C to cool the water to 0°C and have no ice remaining?

11

A liquid is heated at its boiling temperature. Although energy is added to the liquid, its temperature does not increase. Explain.

12

What is the maximum amount of heat energy that you can lose as one gram of water evaporates from your skin?

13

Which is more likely to cause a severe burn, one gram of $H_2O(g)$ at 100°C or one gram of $H_2O(l)$ at 100°C?

14

Liquids used in rocket fuels are passed over the outer wall of the combustion chamber before being fed into the chamber itself. What advantages does this system offer?

15

Which requires more energy, vaporizing one mole of liquid water or decomposing one mole of water by electrolysis? Explain.

16

Suggest possible explanations for the regularity between boiling temperature and molar heat of vaporization for the liquids given in Table 5-2.

17

Two of the methods suggested for conversion of seawater to fresh water are evaporation or freezing of water. Which process uses more energy?

18

Because of its excellent heat conductivity liquid sodium has been proposed as a cooling liquid for use in nuclear power plants.

(a) Over what temperature range could sodium be used in a cooling system designed to operate at one atmosphere pressure?
(b) How much heat would be absorbed per kilogram of sodium to melt the solid when the cooling system is put in operation?
(c) How much heat would be absorbed per kilogram of sodium if the temperature rose too high and the sodium vaporized? Use the data in Tables 5-1 and 5-2.

19

Water is commonly used as a cooling agent in power plants. Repeat Problem 18, using one kilogram of water instead of sodium. Contrast the results for these two coolants.

20

How many grams of ice could be melted by the energy obtained as 18.0 grams of steam is condensed at 100°C and cooled to 0°C? How does the amount of energy obtained as the steam condenses compare to the amount of energy released as the same water is cooled from 100°C to 0°C?

21

A sample of steam at 100°C is condensed to give 180 grams of water, also at 100°C. All of the heat energy is used to vaporize benzene (C_6H_6). This procedure yields 1030 grams of gaseous benzene at its boiling temperature.

(a) Is the molar heat of vaporization of C_6H_6 greater or less than that of H_2O?
(b) What is the value for the molar heat of vaporization for benzene?

22

Why is the boiling temperature for water lower at Denver, Colorado (altitude: 5280 feet) than in Boston, Massachusetts (at sea level)?

23

Both carbon tetrachloride, CCl_4, and mercury, Hg, are liquids whose vapors are poisonous to breathe. If CCl_4 is spilled, the danger can be removed merely by airing the room overnight. If Hg is spilled, it is necessary to pick up the liquid droplets with a "vacuum cleaner" device. Explain.

24

How would the vapor pressure of water measured at 100°C on the moon compare to the vapor pressure of water at the same temperature here on earth?

25

Explain why it is that leftover food placed in a refrigerator tends to dry out if left uncovered.

26

Why do some food production processes, such as the refining of sugar, make use of low pressure evaporation?

27

The vapor pressure of a liquid increases as the temperature increases. State two causes for the increase in vapor pressure.

28

In an experiment, a 500 ml round-bottom flask was filled half-full with water. The water was heated and boiled for a few minutes filling the flask with water vapor. The flask was stoppered and quickly cooled under a stream of cold water. Explain why the water boiled as the flask was cooled.

29

A one gallon can containing a small amount of water was heated. After the water had been boiling for a few minutes, to fill the can with water vapor, a stopper was used to seal the can. The can was then cooled and it collapsed. Explain.

30

Name two solids that have a high enough vapor pressure at room temperature that you can detect their presence by smell.

Solutions, Solubility, and Ions

6

When sand and water are mixed in a beaker, the sand settles to the bottom of the beaker. There are distinct parts to the mixture. We use the word **heterogeneous** to describe this system. The properties change when we go from one part of a heterogeneous mixture to another.

When a small amount of sugar and water are mixed, the sugar dissolves. The solid disappears, becoming part of the liquid. Mixtures of this type are called solutions. We use the word **homogeneous** to describe such a system. The properties are the same every place in a homogeneous system. Both pure substances and solutions are homogeneous. However, a solution differs from a pure substance in that its properties vary, depending on the relative amounts of the substances used in making it. There are three different types of solutions.

A. Gaseous Solutions

All gaseous mixtures are homogeneous. All gaseous mixtures are solutions. Air is a good example of a gaseous solution. Table 6-1 shows the amounts of different gases in a typical sample of dry air.

TABLE 6-1

Composition of Dry Air

Substance		Percent of Molecules
Name	Formula	
Nitrogen	N_2	78.06
Oxygen	O_2	20.99
Argon	Ar	0.93
Carbon dioxide	CO_2	0.03
Trace quantities of neon, helium, krypton, hydrogen, and xenon are present in air. Their total contribution is less than 0.003%.		

U.S. Production, 1965

Argon	71,000 tons
Nitrogen	556,000 tons
Oxygen	2,330,000 tons

The constituents of air can be separated by liquefaction. Large amounts of nitrogen for making fertilizers and of oxygen for the steel industry are obtained from air each year. Except for helium, the noble gases are obtained from air.

B. Solid Solutions

Solid solutions are not as common as gaseous solutions. Crystals are stable because of the regular arrangement of the atoms. A foreign atom interferes with this regular pattern and, therefore, with the crystal stability. As a crystal forms, foreign atoms are usually excluded. That is why crystallization provides a good method for purification.

Metals often form solid solutions. The atoms of one element may enter the crystal of another element if their atoms are about the same size. Gold and copper form solid solutions. Such solid solutions are called **alloys.** Some solid metals dissolve hydrogen or carbon atoms. Steel is iron containing a small amount of dissolved carbon.

C. Liquid Solutions

In the laboratory work for this course you deal most often with liquid solutions. Liquid solutions can be made in many ways. Sometimes two liquids such as water and ethyl alcohol are mixed to form a solution. Some gases, such as NH_3 or CO_2, dissolve in water to give a liquid solution. Most often, liquid solutions are formed when a solid dissolves in water. In all these examples water is called the **solvent.** The substance dissolved in water is called the **solute.**

Solutions are very important to a chemist because so many chemical reactions take place in solution. We will begin our study of solutions by looking at their behavior during phase changes.

6-1 Behavior of Solutions During Phase Changes

When a pure substance such as water is heated, its vapor pressure increases. At 100°C, the vapor pressure of water is 760 mm. At one atmosphere pressure, pure water boils at a constant temperature, 100°C. Let's boil a sample of water until half of it has changed to steam. We can condense the steam to liquid water in a different vessel. If we repeat this experiment with the two samples of water, they show identical behavior.

Pure water freezes at a constant temperature, 0°C. We can freeze half of the water sample to ice, remove the ice, and melt it in another container. If we repeat this experiment with the two samples of water, once again we find that they behave in an identical manner.

What happens if we do the same experiments with a solution made by dissolving a solid in water? Figure 6-1 compares the results of heating pure water and a solution. We can observe several differences. The temperature at which boiling begins in the solution is higher than for pure water. Experiments show that the vapor pressure of an aqueous solution is always less than the vapor pressure of pure water. It is necessary to heat the solution above 100°C to reach a vapor pressure of 760 mm. At one atmosphere pressure, the boiling temperature for the solution must be higher than 100°C. This increase in boiling temperature depends on how much solute is in solution. The more solute dissolved, the higher the boiling temperature.

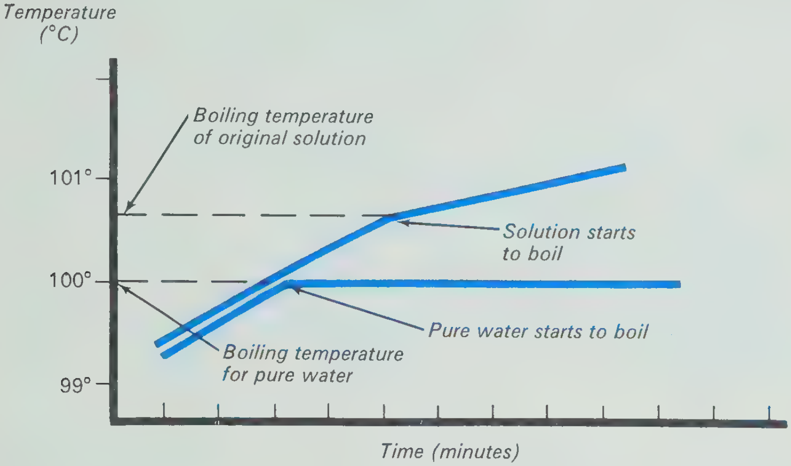


Figure 6-1

Heating curves for pure water and a solution. Heat energy is being added at a constant rate.

As boiling continues, the temperature of pure water stays constant. The temperature of the solution continues to rise during boiling. Let us see if we can find an explanation for this. We can condense the steam from the solution. The liquid we get behaves like pure water. The solute remains behind in the boiling flask. As boiling continues, the relative amount of solute in the solution increases. The boiling temperature of the solution goes up. If we boil off all of the water, solid solute remains behind. We can separate a pure liquid from a solution by evaporating and condensing the vapor that boils off. This process is called **distillation**. Distillation is one way to make fresh water from ocean water. The requirement of about 10 kcal of energy to vaporize one mole of water makes this a rather expensive method. Less expensive methods of obtaining pure water are being explored today. As the world's population continues to increase, the task of converting salty water to pure water looms as one of mankind's most important problems.

Now let us see what happens when a solution is cooled. In Figure 6-3 the solution is compared with pure water as the temperature is lowered. No solid phase appears until the solution is cooled below 0°C. The freezing temperature of the solution is lower than the freezing temperature of pure water. This decrease in freezing temperature depends on how much solute is in the solution. The more solute dissolved, the lower the freezing temperature.

As freezing continues, the temperature of the solution continues to decrease. Perhaps we can find an explanation for this effect. First, separate the solid from the remaining liquid, after about half of the solution has frozen. When we melt this solid, we obtain a liquid which behaves in the same way pure water does on cooling. The

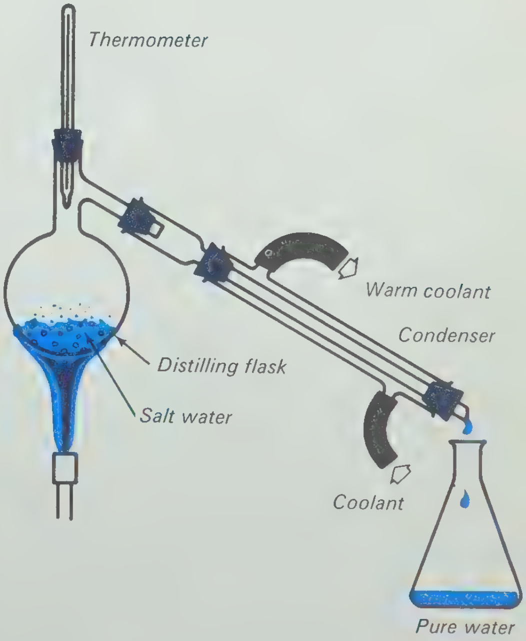


Figure 6-2

A distillation apparatus.

solid that forms during the phase change must contain no solute. The remaining solution must contain all of the dissolved solute. The relative amount of solute in solution has increased. The temperature at which the solution freezes must be decreased. "Antifreeze" substances added to an automobile radiator act this way. They dilute the water in the radiator and lower the temperature at which ice can crystallize from solution. The freezing temperature of the solution will depend on the relative amounts of water and antifreeze.

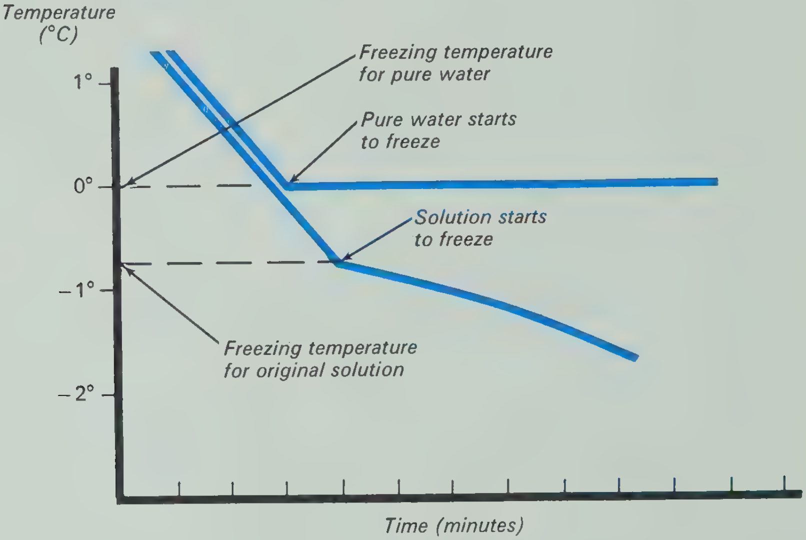


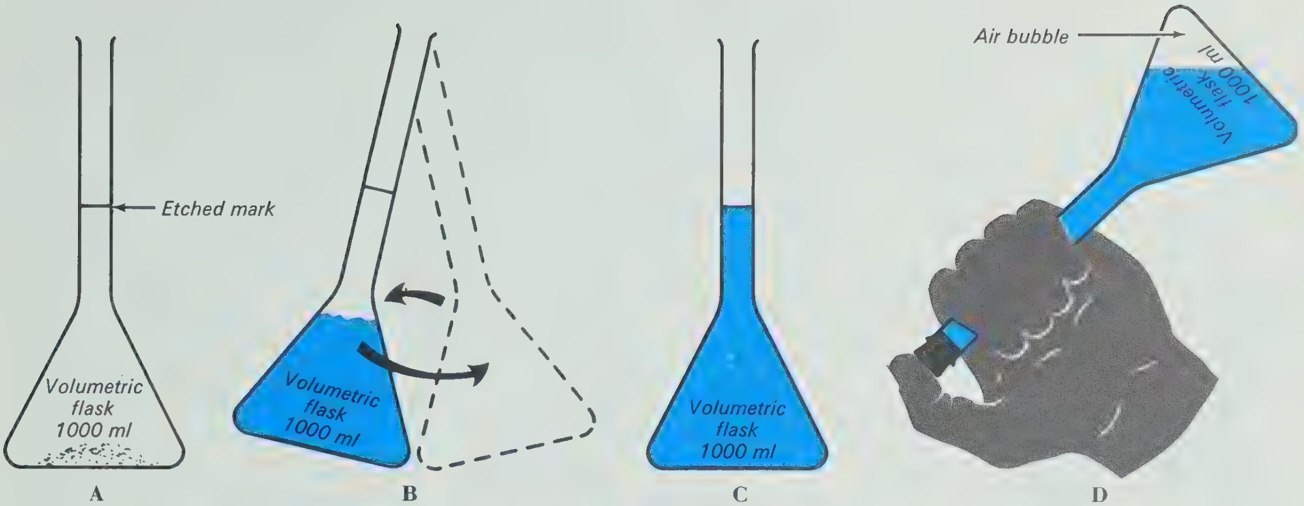
Figure 6-3

Cooling curves for pure water and a solution. Heat energy is being removed at a constant rate.

6-2 Expressing the Concentration of Solutions

The properties of solutions vary depending on the relative amount of solute and solvent used in making them up. Chemists use the term concentration to indicate these relative amounts. You will need only one way of expressing solution concentration in this course: number of moles of solute in one liter of solution. The result is called the **molar concentration** or the **molarity**. A one molar (1 *M*) solution contains one mole of solute in one liter of solution. A two molar (2 *M*) solution contains two moles of solute in one liter of solution. Notice that the concentration of water is not specified. Examples of how to make up some solutions will help you understand what is meant by molarity.

We can start to make a 1.000 *M* solution of NaCl by weighing one mole of salt. From the formula, NaCl, we know that one mole weighs 58.5 grams (23.0 grams + 35.5 grams). We dissolve this salt in some water in a 1-liter volumetric flask as shown in Figure 6-4. This special flask holds 1.000 liter when filled to the mark etched on the neck of the flask. After the salt dissolves, more water is added until the water level almost reaches the etched mark. Now we shake the flask to be sure that the solution is well mixed. Then we can add the last few milliliters of water to make the volume 1.000 liter.


Etched mark
Volumetric flask 1000 ml
A
Volumetric flask 1000 ml
B
Volumetric flask 1000 ml
C
Air bubble
Volumetric flask 1000 ml
D

58.5 grams NaCl

Water added and flask swirled

Water added to etched marking

Flask inverted 15-20 times

Figure 6-4

Preparation of a 1.000 molar NaCl solution.

We can also prepare a 1 M NaCl solution using a 100-ml volumetric flask. The final volume will be 0.1 liter. We need only 0.1 mole of NaCl. We weigh 5.85 grams of NaCl, place it in the flask, dissolve it and add water to the 100 ml mark. These examples show that

$$\text{Molarity} = \frac{\text{number of moles (solute)}}{\text{liters of solution}}$$

EXERCISE 6-1

What mass of $AgNO_3$ is needed to make 1 liter of 1 M solution?

EXERCISE 6-2

What mass of $AgNO_3$ is needed to make 100 ml of 2 M solution?

EXERCISE 6-3

You have 8.4 grams of solid sodium bicarbonate, $NaHCO_3$. How many moles of solid is this? How much 1 M solution can be made with this amount of $NaHCO_3$?

6-3 Solubility

Let's add a small amount of a solid to a liquid, keeping the temperature constant. The solid begins to dissolve and the concentration of the solution rises. After all of the solid has dissolved, the concentration remains constant, fixed by the amount of dissolved solid and the volume of the solution. If more solid is now added, the concentration will rise further. Finally, however, the addition of more solid no longer raises the concentration of dissolved material. When a fixed amount of liquid has dissolved all of the solute that it can, the concentration reached is called the **solubility** of that solute. A solution that will dissolve no more solute is said to be **saturated.**

The solubilities of solids in liquids vary widely. For example, sodium chloride dissolves in water at 25°C until the concentration is about six moles per liter. The solubility of NaCl in water is 6 M at 25°C. In contrast, only a small amount of sodium chloride dissolves in ethyl alcohol at 25°C. The solubility is 0.009 M. Even in a particular liquid, solubilities differ over wide limits. The solids calcium chloride, $CaCl_2$, and silver nitrate, $AgNO_3$, have solubilities in water exceeding one mole per liter. The solid, silver chloride, AgCl, has a solubility in water of only 10^{-5} mole per liter.

Temperature influences how much solid will dissolve and how fast. In general, the amount and rate of dissolving will go up when temperature is raised.

Because of this range of solubilities, the word soluble does not have a precise meaning. There is an upper limit to the solubility of the most soluble solid. On the other hand, even the least soluble solid furnishes a few dissolved particles per liter of solution. We use glass containers for much of our laboratory work in chemistry because glass has such low solubility in water. Yet in some experiments, this solubility must be taken into consideration.

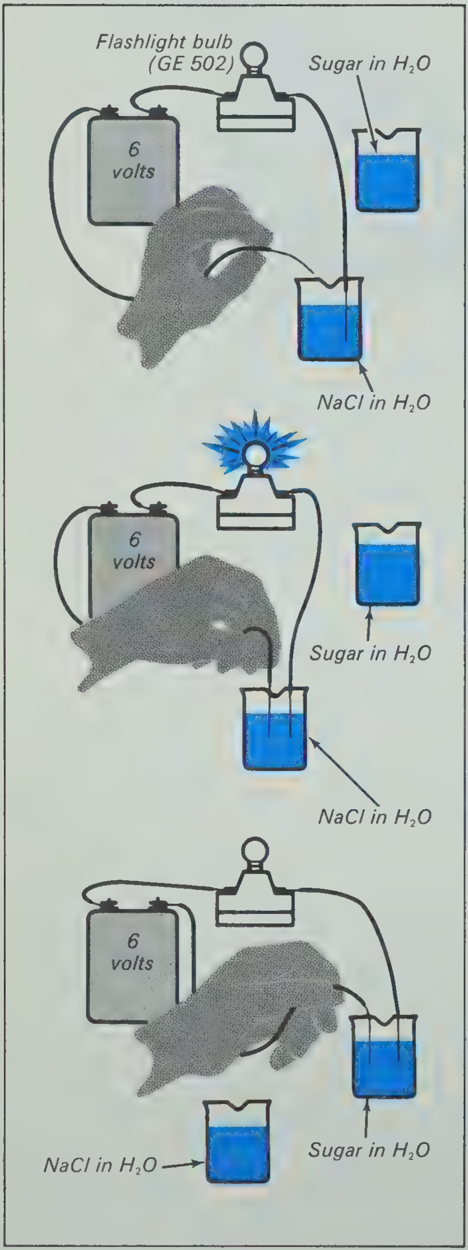


Figure 6-5

Salt solution conducts electricity; sugar solution does not.

6-4 Variations Among Properties of Solutions

The differences among solutions can be very great. We can demonstrate these differences with five substances: sodium chloride, sugar, iodine, ethyl alcohol, and water. Let us use the liquids, water and ethyl alcohol, as solvents in making up a set of solutions.

First, we can investigate the solubility of the three solids in each solvent. By adding a small crystal of each solid to one milliliter of liquid, we find out that sugar dissolves in water and in ethyl alcohol. Sodium chloride dissolves readily in water but not in ethyl alcohol. Iodine, on the other hand, dissolves in ethyl alcohol but not appreciably in water. The solvent properties of the two liquids are different.

The experiment just described gives us four solutions containing a substantial amount of solute.

I	II	III	IV
Sugar in water	Sugar in ethyl alcohol	Sodium chloride in water	Iodine in ethyl alcohol

Of these four solutions, IV is readily distinguished. It has a dark brown color. The other three, like many solutions, are colorless. They can be distinguished by taste, but chemists have safer ways of telling them apart. Many solutions differ in the way they conduct an electric current. Figure 6-5 shows this measurement. The two sugar solutions have almost the same conductivity properties as the pure solvents. Their conductivity is very low. In marked contrast solution III conducts electric current much more readily than does pure water. Differences in electrical conductivity are used to distinguish one solution from another.

You are familiar with many electrical devices. They surround you at home and at school. They furnish power, light, and means of communication. Try to name several electrical phenomena that you have observed. Does your list include the following?

(1) The heat generated by an electric current passing through the heating element of an electric stove.

(2) The light emitted by the filament of an electric light bulb as electric current passes through it.

(3) The work done by an electric motor when electric current passes through its coils.

(4) The attraction of a comb for your hair on a dry day.

(5) A flash of lightning.

The interest of a chemist in the electrical nature of matter goes far deeper than this. We shall find that an understanding of electrical behavior furnishes a key to the explanation of chemical properties. We shall also find that electrical effects aid us in predicting molecular formulas, in explaining chemical reactions, and in understanding energy changes that accompany them. In order to understand the electrical behavior of matter, we must find out what is meant by electric charge.

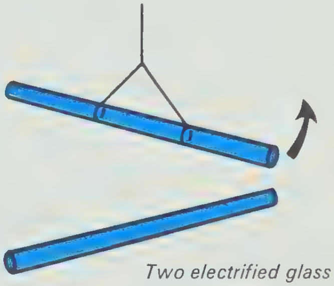
6-5 Electric Charge

Rub a glass rod with a piece of silk and hang the rod up with a silk thread. Then rub a second glass rod and slowly bring it near to the first rod. As the two rods get close to each other, the first one moves away. It is repelled.

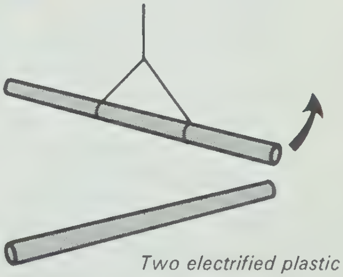
Now repeat this experiment with two plastic rods, rubbed with a piece of fur, instead of silk. Once again, the rods move apart as they are brought near each other.

If we bring the plastic rod close to the suspended glass rod, the two rods move toward each other, not away. The two rods attract one another. These experiments are shown in Figure 6-6.

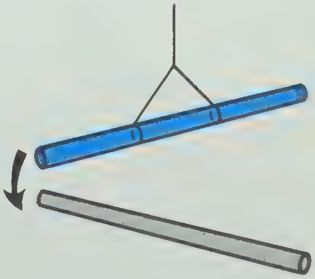
We use the word "electrified" to describe the condition of these rods after they have been rubbed vigorously. We can explore what happens with many different materials. Our experimental results always fall into two classes. Objects of the same material that have been electrified by the same procedure always repel each other. Objects of different materials may attract or repel each other. We find that electrified objects fall into two groups. Only two electrified states exist. One is like the state of the electrified glass rod. The other is similar to the state of the electrified plastic rod. We say that any object that behaves the way the glass rod does is **positively**



Two electrified glass rods repel each other



Two electrified plastic rods repel each other



Electrified glass rod is attracted to electrified plastic rod.

Figure 6-6

Electrical attraction and repulsion.

charged. Any object that behaves the way the plastic rod does is **negatively charged.**

Today it is easy to place an electric charge on different objects. You are familiar with the storage battery in an automobile or the dry cells in a flashlight. These are sources of electrical energy. A battery has two terminals, one marked "plus" and the other marked "minus." We can give an electric charge to an object by connecting it to one of the battery terminals.

A famous physicist, Robert Millikan, carried out a very precise experiment to measure electric charge. This experiment is diagrammed in Figure 6-7. Two plates are connected to opposite terminals of a battery. One plate acquires a positive electric charge. The other plate acquires a negative electric charge. Tiny droplets of oil or mercury are sprayed into the upper section of the apparatus. As these droplets fall through the air, some of them acquire an electric charge. If a charged droplet floats into the space between the charged plates, we can keep it from rising or falling by adjusting the charges on the two plates. This means a balance has been achieved between the gravitational forces which would make the particle fall and electrical forces which would make the particle move back to the upper plate.

Millikan carried out thousands of such experiments. He measured the electric charge that had to be placed on the parallel plates so that the droplets would hang suspended. Sometimes he found that the droplet had a positive charge. Sometimes it had a negative charge. He established that there is a smallest electric charge, either positive or negative. This is called the *unit charge of electricity*. We know that matter comes in units called atoms. Electric charge also comes in units. You can have one or two or any other whole number of units of electric charge. Particles with half or three quarters of a unit of electric charge are never found.

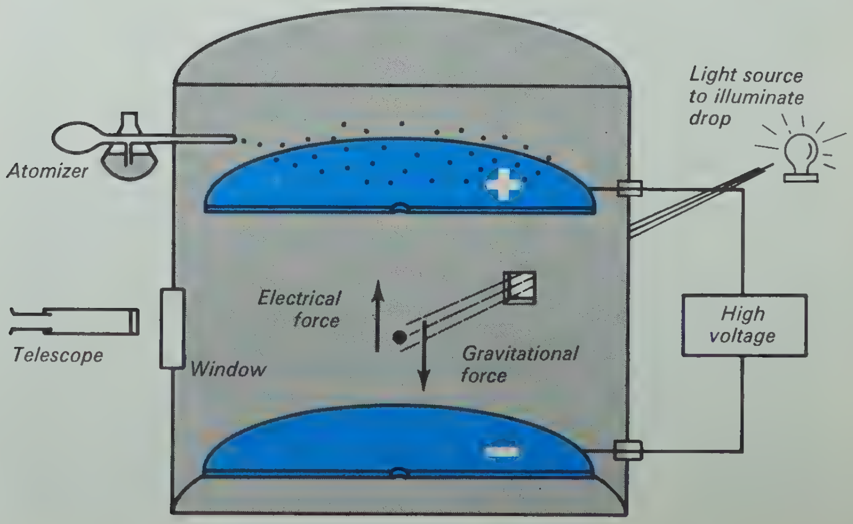


Figure 6-7

Cross-sectional view of apparatus for Millikan oil drop experiment.

6-6 The Electron-Proton Model

The new facts about electrical phenomena can be made part of our particle model. Let us propose that matter is made up of two kinds of particles which carry the property of electric charge. The particle which has one unit of negative electric charge is called the **electron.** The particle which has one unit of positive electric charge is called the **proton.**

Let us see what our model looks like now. If an object has the same number of electrons and protons, then the amount of negative electric charge would be equal to the amount of positive electric charge. We say that the object is **electrically neutral.** It has **zero electric charge.**

Neutral atoms or molecules have zero electric charge. *They have equal numbers of electrons and protons.* The following examples will illustrate this point.

The H atom, the O atom, and the H_2O molecule have zero charge. Chemists know that the H atom is made up of one electron and one proton. The oxygen atom consists of eight electrons and eight protons. We represent each of these atoms, in Figure 6-8, as a neutral particle. The H_2O molecule must have ten electrons and ten protons, coming from the two H atoms plus one O atom. This is also shown in Figure 6-8. The important point right now is the zero value for total electric charge. Particles having equal numbers of electrons and protons have zero electric charge. The atom or molecule is electrically neutral.

We shall see later that it is easy to add an electron to some atoms or molecules. In other instances it is easy to remove an electron from an atom or molecule. When these processes take place, particles are formed with different numbers of electrons and protons. There is a net electric charge on these particles. Chemists have given the name **ions** to charged particles. Here are two examples. The symbol e^- represents one electron and p^+ represents one proton.

H atom contains

1 electron 1 proton	symbolized	$1\ e^-$ $1\ p^+$	gives zero electric charge

O atom contains

8 electrons 8 protons	symbolized	$8\ e^-$ $8\ p^+$	gives zero electric charge

H_2O molecule contains 2 H atoms + 1 O atom

$1\ e^-$ $1\ p^+$	$8\ e^-$ $8\ p^+$	$1\ e^-$ $1\ p^+$	gives zero electric charge

$$\text{Chlorine atom} + \text{electron} \longrightarrow \text{chloride ion}$$

$$\mathrm{Cl} + e^- \longrightarrow \mathrm{Cl}^-$$

$$\begin{array}{c}17\,e^-\\17\,p^+\end{array} + e^- \longrightarrow \begin{array}{c}18\,e^-\\17\,p^+\end{array}$$

Notice that the electric charge on the chloride ion is 1 −. Seventeen protons plus eighteen electrons give a net charge of 1 −.

$$(17+) + (18-) = (1-)$$

The sodium atom loses an electron to become a sodium ion.

$$\text{Sodium atom} \longrightarrow \text{sodium ion} + \text{electron}$$

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + e^-$$

$$\begin{array}{c}11\,e^-\\11\,p^+\end{array} \longrightarrow \begin{array}{c}10\,e^-\\11\,p^+\end{array} + e^-$$

The net electric charge for the sodium ion is 1 +.

6-7 Electric Properties of Condensed Phases

Now we are ready to investigate behavior of condensed phases that shows evidence of the presence and movement of electric charge. The movement of electric charge is called an **electric current.** When we say electric current flows through a solution, we mean there is a movement of electric charge through the solution. We want to see how this charge moves.

Water is a very poor conductor of electricity. Yet when sodium chloride, table salt, dissolves in water, the solution conducts readily. The dissolved sodium chloride must be responsible. How does the dissolved salt affect the solution so that electric charge can move through the liquid? One possibility is that ions are present in the salt solution. The movement of these charged particles through the solution could account for the electric current. Salt has the formula NaCl. For every sodium atom there is one chlorine atom. Chemists have discovered that the ions Na^+ and Cl^- are present when NaCl is dissolved in water. We can write this as an equation.

$$\mathrm{NaCl}(\text{solid}) + \text{water} \longrightarrow \mathrm{Na}^+(\text{in water}) + \mathrm{Cl}^-(\text{in water})$$

Chemists usually omit the term "water" on the left side of this equation. Its presence is implied by the symbols on the right side of the equation. The expression "in water" is further shortened to "aq," meaning **aqueous.** The equation is usually written

$$\mathrm{NaCl(s)} \longrightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

The solid dissolves, forming the charged particles $\mathrm{Na^+(aq)}$ and $\mathrm{Cl^-(aq)}$. They can move about in the solution independently. Their attraction for each other is reduced because they are surrounded by many water molecules. Ions with positive charge are called **cations.**

Ions with negative charge are called **anions.** An electric current can pass through the solution by means of the movement of these ions. The $Cl^-(aq)$ ions move in one direction, causing negative charge to move that way. The $Na^+(aq)$ ions move in the opposite direction, causing positive charge to move this way. These movements carry charge through the solution, and electric current flows.

Sugar dissolves in water. The solution conducts electric current no better than does pure water. We conclude that no charged particles are present in a sugar solution. No ions are formed.

Calcium chloride, $CaCl_2$, is another crystalline solid that dissolves readily in water. The solution conducts electric current. Calcium chloride is, in this regard, like sodium chloride and unlike sugar. Ions are present in solution when calcium chloride dissolves in water. The equation for the reaction is

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2\,Cl^-(aq)$$

The calcium ion, $Ca^{2+}(aq)$, has twice the positive charge of $Na^+(aq)$. The chloride ion that forms, $Cl^-(aq)$, behaves in the same way as the negative ion that is present in the sodium chloride solution. Because of that, we write $2\,Cl^-$ and not Cl_2^{2-}, in the equation representing the dissolving of calcium chloride. A 1 *M* solution of calcium chloride contains two moles of chloride ion per liter of solution.

EXERCISE 6-4

A neutral calcium atom has 20 electrons and 20 protons. Show the formation of Ca^{2+} as an electron loss process.

Silver nitrate, $AgNO_3$, is a third solid substance that dissolves in water to give a conducting solution. The ions formed are silver ions, $Ag^+(aq)$, and nitrate ions, $NO_3^-(aq)$. The reaction is

$$AgNO_3(s) \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

The aqueous silver ion is a silver atom with the positive charge of a proton. It carries the same charge as an aqueous sodium ion. The aqueous nitrate ion carries the negative charge of an electron. It has the same charge as the aqueous chloride ion. This time, however, the negative charge is carried by a group consisting of one nitrogen and three oxygen atoms. Since this group, NO_3^-, remains together throughout many chemical reactions, acting as a unit, it has been given a distinctive name, **nitrate ion.** There are many other examples of polyatomic ions.

EXERCISE 6-5

The solids listed below dissolve readily in water to give solutions that conduct electricity. For each substance write an equation to represent what happens. The four ions (sulfate, ammonium, carbonate, and hydrogen carbonate) act as units in the same way nitrate ion does. What electric charges would each of these ions have?

(Exercise 6-5 continued on p. 94.)

(Exercise 6-5 continued from p. 93.)

Na_2SO_4	Sodium sulfate
NH_4Cl	Ammonium chloride
$(NH_4)_2CO_3$	Ammonium carbonate
$NaHCO_3$	Sodium hydrogen carbonate
$CuCl_2$	Cupric chloride

The electrical conductivity of an aqueous solution depends on how much solute is dissolved in the water and also on whether ions are formed. A solution containing 0.1 mole NaCl per liter exhibits higher conductivity than a solution containing 0.01 mole NaCl per liter. The amount of current conducted depends on the concentration of ions.

6-8 Ionic Solids

The solids sodium chloride, calcium chloride, and silver nitrate are similar. They all dissolve in water to form aqueous ions and give conducting solutions. These solids are called **ionic solids.** Let us see what that means.

The sodium chloride crystal contains an equal number of sodium atoms and chlorine atoms. They are not present as molecules. On the basis of much experimental evidence, chemists have concluded that sodium chloride crystals are built up of sodium ions, Na^+, and chloride ions, Cl^-, rather than of neutral atoms or molecules. The numbers of Na^+ and Cl^- ions must be equal because the entire crystal is electrically neutral. There is electrical attraction between these oppositely charged particles. This attraction between positive and negative ions accounts for the bonding in an ionic solid.

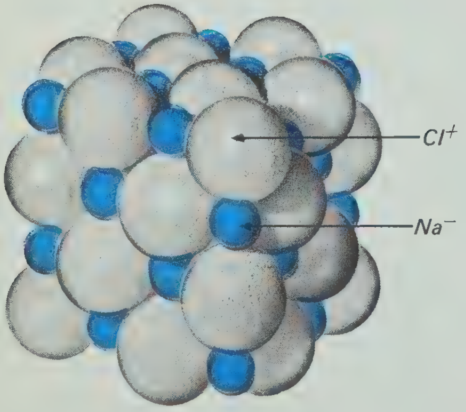


Figure 6-8

The face-centered cubic structure of Na^+Cl^-.

We use the formula NaCl to represent the composition of such a solid. The formula NaCl shows only the simplest ratio of the number of atoms in the compound. It is called an **empirical formula.** Figure 6-9 shows the arrangement of the ions in the sodium chloride crystal. The ions are arranged in layers. A layer in the interior of a crystal has a similar layer in front of it and another behind it. These layers are displaced so that a Cl^- ion lies in front of each Na^+ ion and a Cl^- ion lies behind each Na^+ ion. Each ion is surrounded by six oppositely charged ions. We call this arrangement the **sodium chloride structure.** Many other ionic solids have the same crystal structure. Among them are LiF, KCl, and MgO.

When an ionic solid such as sodium chloride is melted, the molten salt conducts electric current. The conductivity is like that of an aqueous salt solution. Na^+ and Cl^- ions are present. The extremely high melting temperature (1081°K) shows that a large kinetic energy is needed to break down the NaCl crystalline arrangement to free the ions so that they can move. In contrast, solid sodium chloride dissolves readily in water at room temperature and without a large heat effect. A reasonable interpretation is that the water interacts strongly with the ions. Aqueous ions are about as stable as ions in the crystal. In fact, water interacts so strongly with ions that some molecular solids dissolve in water to form conducting solutions.

Copper melts at 1356°K.

For example, solid hydrogen chloride, HCl(s), is a molecular crystal similar to the ice crystal. The solid is made up of HCl molecules. It is not made of ions like the ionic solid sodium chloride. Hydrogen chloride crystals melt at −111°C and vaporize at −84°C to give gaseous diatomic molecules which are not ionic. Yet HCl dissolves in water to form a conducting solution containing hydrogen ions, $H^+(aq)$, and chloride ions, $Cl^-(aq)$. We cannot safely interpret the conductivity of an aqueous solution to mean that the solid dissolved was an ionic solid. We can, however, state the opposite: when an ionic solid dissolves in water, a conducting solution is obtained.

6-9 Types of Compounds That Are Electrolytes

Substances that dissolve in water to give conducting solutions are called **electrolytes.** We begin by looking for some regularities in the behavior of solutions of electrolytes. The observed properties suggest that there are three classes of electrolytes. Chemists use the words **acid, base,** and **salt** to identify these three classes. Let's list the properties of aqueous solutions for each class of compound.

	ACIDS
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
$HC_2H_3O_2$	Acetic acid
H_3PO_4	Phosphoric acid

PROPERTIES OF AN ACIDIC SOLUTION

1. Tastes sour.
2. Reacts with metals such as zinc or magnesium, with liberation of hydrogen.
3. The dye, litmus, becomes red in color when added to an acidic solution.
4. Conducts electricity.

	BASES
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
NH_4OH	Ammonium hydroxide
$Ca(OH)_2$	Calcium hydroxide
$Ba(OH)_2$	Barium hydroxide

PROPERTIES OF A BASIC SOLUTION

1. Tastes bitter, feels slippery.
2. The dye, litmus, becomes blue in color when added to a basic solution.
3. Reacts with an acidic solution, to destroy or neutralize the properties characteristic of an acid.
4. Conducts electricity.

The reaction between an acid and a base is one of the oldest chemical reactions known to man. We can write a general equation for this reaction.

$$\text{Acid} + \text{Base} \longrightarrow H_2O + \text{Salt}$$

When the solution is heated, water can be driven off. A compound, called a **salt,** crystallizes from solution. Here are a few equations to show salt formation.

$$\text{Acid} + \text{Base} \longrightarrow \text{Water} + \text{Salt}$$

$$HCl(aq) + NaOH(aq) \longrightarrow H_2O + NaCl(aq)$$

$$H_2SO_4(aq) + KOH(aq) \longrightarrow H_2O + KHSO_4(aq)$$

$$H_2SO_4(aq) + 2\ KOH(aq) \longrightarrow 2\ H_2O + K_2SO_4(aq)$$

$$HC_2H_3O_2(aq) + NH_4OH(aq) \longrightarrow H_2O + (NH_4)(C_2H_3O_2)(aq)$$

We have chosen to write NaOH(aq) and NaCl(aq). It would be somewhat better to show that these compounds exist in water as hydrated ions, $Na^+(aq)$, $OH^-(aq)$, $Cl^-(aq)$. However, it is easier at this stage to see what happens in the reaction when empirical formulas are used instead of ionic formulas.

	SALTS
NaCl	Sodium chloride
$KHSO_4$	Potassium hydrogen sulfate
K_2SO_4	Potassium sulfate
$(NH_4)(C_2H_3O_2)$	Ammonium acetate
$AgNO_3$	Silver nitrate
$CaCl_2$	Calcium chloride

PROPERTIES OF A SALT SOLUTION

1. Tastes salty.
2. The dye, litmus, usually does not change color when added to a solution.
3. Conducts electricity, if salt is soluble.

Sulfuric acid, H_2SO_4, reacts with a base like KOH to give two different salts. The normal salt, K_2SO_4, forms when 2 moles of base react with 1 mole of acid. The acid salt, $KHSO_4$, forms when 1 mole of base reacts with 1 mole of acid. $KHSO_4$ and K_2SO_4 are white crystalline solids. Like crystalline NaCl, these salts have an ionic structure in the solid.

We will return to a more detailed discussion of acids and bases in Chapter 14. Now we finish this chapter by considering the solubility of ionic compounds.

6-10 Solubility of Ionic Compounds

Experiments show that some ionic compounds are very soluble in water while other ionic compounds, such as AgCl, do not dissolve to any appreciable extent in water. We can summarize in a qualitative fashion the solubilities for a large number of substances. We will say that a substance is soluble if we can make an aqueous solution with concentration greater than 0.1 *M*. Table 6-2 summarizes the solubility in water of many ionic compounds that you are likely to encounter in your laboratory program. We have tried to emphasize the regularities you would find. An important use of these solubility guides is the separation of one substance with low solubility from a substance with high solubility. We will discuss this again in Chapter 13.

Some cations form soluble compounds with all of the anions commonly encountered in the laboratory. These cations are the ammonium ion, NH_4^+, and the ions of the alkali metals, Li^+, Na^+, K^+, Rb^+, and Cs^+.

Some anions form soluble compounds with all of the cations commonly found in the laboratory. Almost all compounds containing nitrate ion, NO_3^-, or acetate ion, $C_2H_3O_2^-$, are soluble in water at room temperature.

TABLE 6-2

Solubility of Ionic Compounds in Water

Negative Ions (anions)	+	Positive Ions (cations)	form	Compounds which are:
All		Alkali ions (Li^+, Na^+, K^+, Rb^+, Cs^+)		Soluble*
All		Ammonium ion, NH_4^+		Soluble
Nitrate, NO_3^-		All		Soluble
Acetate, $C_2H_3O_2^-$		All		Soluble
Chloride, Cl^- Bromide, Br^- Iodide, I^-		Ag^+, Pb^{2+}, Hg_2^{2+}, Cu^+ All others		Not soluble Soluble
Sulfate, SO_4^{2-}		Ba^{2+}, Sr^{2+}, Pb^{2+}, Ca^{2+} All others		Not soluble Soluble
Sulfide, S^{2-}		Alkali ions, NH_4^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} All others		Soluble Soluble Not soluble
Hydroxide, OH^-		Alkali ions, NH_4^+, Sr^{2+}, Ba^{2+} All others		Soluble Soluble Not soluble
Phosphate, PO_4^{3-} Carbonate, CO_3^{2-} Sulfite, SO_3^{2-}		Alkali ions, NH_4^+ All others		Soluble Not soluble

* Soluble means more than 0.1 mole will dissolve per liter.

6-11 Review

Solutions are homogeneous mixtures of two or more pure substances. Although there are gaseous solutions and solid solutions, chemists encounter liquid solutions far more frequently. In aqueous solutions, water is usually considered to be the **solvent**. The substances dissolved in water are called **solutes.**

Comparison of the behavior of solutions and of pure substances during phase changes brings out some important differences. In most cases the boiling temperature of a solution is higher than the boiling temperature of the pure solvent. Similarly, in most cases the freezing temperature of a solution is lower than the freezing temperature of the pure solvent.

In this chapter we have considered experiments which show that some solutions are good conductors of electricity while others are poor conductors of electricity. In searching for an explanation for the results of these experiments, we have examined what the term electric charge means. Chemists have found that some substances dissolve in water to form electrically charged particles called **ions.** Other substances dissolve in water without forming ions. The conduction of electric charge through a solution can be accomplished by ions moving through the solution.

Substances that dissolve in water to give conducting solutions are called **electrolytes.** Chemists find it convenient to classify electrolytes as acids, bases, or salts.

Questions and Problems for Chapter 6

1

List three heterogeneous materials.

2

List three homogeneous materials.

3

Which of the following statements about seawater is FALSE?

(a) It boils at a higher temperature than pure water.
(b) It melts at a lower temperature than pure water.
(c) The boiling temperature rises as the liquid boils away.
(d) The melting temperature falls as the liquid freezes.
(e) The density is the same as that of pure water.

4

Early gold miners collected very fine gold dust from their sluice boxes by dissolving it in mercury. How do you think the gold was then separated from the mercury?

5

Would ocean water in which ice has been formed and then removed be a better source of salt than untreated ocean water? Explain.

6

How many grams of methanol, CH_3OH, must be added to 2.00 moles of H_2O to make a solution containing equal numbers of H_2O and CH_3OH molecules? How many molecules (of all kinds) does the resulting solution contain?

7

How many grams of ammonium chloride, NH_4Cl, are present in 0.30 liter of a 0.40 *M* NH_4Cl solution?

Answer: 6.4 grams.

8

Write directions for preparing the following aqueous solutions:

(a) 1.0 liter of 1.0 *M* lead nitrate, $Pb(NO_3)_2$, solution
(b) 2.0 liters of 0.50 *M* ammonium chloride, NH_4Cl, solution
(c) 0.50 liter of 2.0 *M* potassium chromate, K_2CrO_4, solution

9

How many liters of 0.250 *M* K_2CrO_4 solution contain 38.8 grams of K_2CrO_4?

10

Which has the greater solubility in water:

(a) pepper or salt
(b) CO_2 or N_2
(c) oil or molasses
(d) limestone or granite

11

One liter of saturated calcium carbonate solution contains 0.0153 gram at 25°C. What is the solubility of $CaCO_3$ in moles/liter?

12

Name three chemicals that readily dissolve in water. Name three that scarcely dissolve at all.

13

List three properties of a solution you would expect to vary as the concentration of the solute varies.

14

Give two forces other than electric that are felt at a distance.

15

Why do two electrically neutral objects with mass attract each other?

16

Why do scientists claim there are only two kinds of electric charge?

17

The following 6 measurements were obtained during a Millikan oil-drop experiment. They represent the electric charge on the drop.

4.83×10^{-19} coulomb
3.24
9.62
6.44×10^{-19} coulomb
4.80
1.62

(a) Might one of these values correspond to the unit electric charge? Which one? Why?
(b) Can you think of an argument to rule out the value 0.81×10^{-19} coulomb as the unit electric charge?

18

A neutral atom of barium has 56 electrons. Barium forms a 2+ ion. How many protons does a barium ion have? How many electrons in the 2+ ion? Show the formation of the ion as an electron loss process.

19

A neutral fluorine atom has 9 protons. Fluorine, F, forms an ion with 1− charge. How many electrons does a fluoride ion, F^-, have? Starting with F_2, show the formation of F^- as an electron gain process. Check to see that charge is balanced.

20

What would you expect the empirical formula for barium fluoride to be?

21

Each of the following ionic solids dissolves in water to form conducting solutions. Write equations for each reaction.

(a) potassium chloride, KCl
(b) sodium nitrate, $NaNO_3$
(c) calcium bromide, $CaBr_2$
(d) lithium iodide, LiI

22

A chloride of iron called ferric chloride, $FeCl_3$, dissolves in water to form a conducting solution containing ferric ions, Fe^{3+}, and chloride ions, Cl^-.

(a) Write the equation for this reaction.
(b) If 0.10 mole of $FeCl_3$ is dissolved in 1.0 liter of water, what is the concentration of ferric ion and of chloride ion?

Answer: Concentration of $Fe^{3+} = 0.10\ M$.
Concentration of $Cl^- = 0.30\ M$.

23

The salt ammonium sulfate, $(NH_4)_2SO_4$, dissolves in water to form a conducting solution containing ammonium ions, NH_4^+, and sulfate ions, SO_4^{2-}.

(a) Write the balanced equation for the reaction when this ionic solid dissolves in water.

(b) Verify the conservation of charge by comparing the charge of the reactant to the sum of the charges of the products.
(c) Suppose 1.32 grams of ammonium sulfate is dissolved in 0.500 liter of water. Calculate the concentrations of $NH_4^+(aq)$ and $SO_4^{2-}(aq)$.

24

For 1.00 liter of solution made from 0.100 mole of ferric chloride, $FeCl_3$, and 0.100 mole of ammonium chloride, NH_4Cl, calculate the molar concentrations of the three ions Fe^{3+}, NH_4^+, and Cl^-.

25

Assume the following compounds dissolve in water to form separate, mobile ions in solution. Write the formulas and the names for the ions that can be expected.

(a) HI
(b) $CaCl_2$
(c) Na_2CO_3
(d) $Ba(OH)_2$
(e) KNO_3
(f) NH_4Cl

26

Write the equation for the reaction that occurs when each of these electrolytes is dissolved in water.

(a) lithium hydroxide (solid)
(b) nitric acid (liquid)
(c) potassium sulfate (solid)
(d) sodium nitrate (solid)
(e) ammonium iodide (solid)
(f) potassium carbonate (solid)

27

What ion will all the acids listed on page 95 form?

28

What ion will all the bases listed on page 95 form?

29

In Experiment 16 you mixed lead nitrate and sodium iodide solutions. Write an equation for the reaction that occurred. Show only the predominant species.

30

Write equations for the reactions between aqueous bromide ions and:

(a) aqueous lead ions
(b) aqueous silver ions

Use Table 6-2 to help you decide how to write these equations.

31

When solutions of barium chloride, $BaCl_2$, and potassium chromate, K_2CrO_4, are mixed, the following reaction occurs:

$$2\,K^+(aq) + CrO_4^{2-}(aq) + Ba^{2+}(aq) + 2\,Cl^-(aq) \longrightarrow BaCrO_4(s) + 2\,K^+(aq) + 2\,Cl^-(aq)$$

(a) Show how charge is conserved.
(b) Rewrite the equation showing predominant species only. Is charge conserved when the equation is written this way?
(c) Suppose 1.00 liter of 0.500 *M* $BaCl_2$ is mixed with 1.00 liter of 0.200 *M* K_2CrO_4. Assume that $BaCrO_4$ has negligible solubility. Calculate the concentrations of all ionic species present when precipitation is complete.

Answer: Concentration K^+ = 0.200 *M*
Concentration Cl^- = 0.500 *M*
Concentration CrO_4^{2-} = negligible
Concentration Ba^{2+} = 0.150 *M*

32

Predict what would happen if equal volumes of 0.2 *M* Na_2SO_3 and 0.2 *M* $MgSO_4$ were mixed. If a reaction takes place, write the net ionic equation.

33

Using Table 6-2 make a statement about the solubilities of the compounds containing the following ions.

ANION	CATIONS
(a) carbonate, CO_3^{2-}	alkali ions, (Li^+, Na^+, K^+, Rb^+, Cs^+)
(b) carbonate, CO_3^{2-}	alkaline earth ions, (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+})
(c) sulfide, S^{2-}	alkaline earth ions, (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+})

34

Write an empirical formula for each of the following compounds and indicate which have low solubilities.

(a) silver sulfide
(b) potassium sulfide
(c) ammonium sulfide
(d) nickel sulfide
(e) ferrous sulfide
(f) ferric sulfide

35

Write a net ionic equation for any reaction that will occur upon mixing equal volumes of 0.2 *M* solutions of the following pairs of compounds.

(a) silver nitrate and ammonium bromide
(b) $SrBr_2$ and $NaNO_3$
(c) sodium hydroxide and aluminum chloride
(d) barium chloride and sodium sulfate

Answer: (a) $Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$

36

What ions could be present in a solution if samples of it gave:

(a) a precipitate when either $Cl^-(aq)$ or $SO_4^{2-}(aq)$ is added?
(b) a precipitate when $Cl^-(aq)$ is added but none when $SO_4^{2-}(aq)$ is added?
(c) a precipitate when $SO_4^{2-}(aq)$ is added but none when $Cl^-(aq)$ is added?

37

Use Table 6-2 to decide which of the following soluble substances would permit a separation of aqueous magnesium from barium ions. For those that are effective, write the equation for the reaction that occurs.

(a) ammonium carbonate
(b) sodium bromide
(c) potassium sulfate
(d) sodium hydroxide

38

Some 2 *M* NaBr solution is added to a sample which is 0.1 *M* in each of the following ions, Ag^+, Cu^+, Fe^{2+}, and Ca^{2+}. Precipitate *A* forms and is filtered out. A sulfide solution is added to the filtrate and black precipitate *B* forms. This precipitate is removed by filtration and 2 *M* sodium carbonate solution is added, giving precipitate *C*. What is the composition of *A*, *B*, and *C*?

Order Among Atoms

7

During the nineteenth century, chemists made a large number of careful observations on the elements and their compounds. A major goal was to find an arrangement of the elements that would provide some organization for these observations. This search by chemists is in many ways like that of the lost child in the fable. Some of the first regularities proved too limited in nature. Other proposals were shown to be incorrect. Step by step, better arrangements were achieved.

For many years chemists recognized differences between metals and nonmetals. Table 7-1 contrasts the properties that can be observed for these two classes of materials.

TABLE 7-1

Comparison of the General Properties of
Metals and Nonmetals

Metals	Nonmetals
Solids	Often gases and liquids
High density	Low density
High melting temperature	Low melting temperature
Shiny	Not shiny
Good conductors of heat and electricity	Poor conductors of heat and electricity
Oxides usually soluble in acid solutions	Oxides usually soluble in basic solutions

It was difficult to decide how to classify some substances. Mercury has many metallic properties, but it is a liquid at room temperature. Carbon, in the form of graphite, is a good conductor of electricity, while carbon in the form of diamond is a poor conductor. Even though graphite and diamond have very high melting temperatures, chemists consider carbon to be a nonmetal.

By 1800 chemists knew that many metals and nonmetals reacted with oxygen in the air. They also could establish the ratio between the number of moles of an element and the number of moles of oxygen in the compounds that formed. A few examples will help you see what this statement means. The symbol M will be used to represent any element except oxygen. In modern terms the reactions can be written as in Table 7-2.

TABLE 7-2

Formation of Oxides

Reaction	Ratio M/O in Oxide
$4\,M + O_2 \longrightarrow 2\,M_2O$	$^2/_1$
$2\,M + O_2 \longrightarrow 2\,MO$	$^1/_1$
$4\,M + 3\,O_2 \longrightarrow 2\,M_2O_3$	$^2/_3$
$M + O_2 \longrightarrow MO_2$	$^1/_2$

Some elements form oxides with the formula M_2O. Other elements form oxides with a different M/O ratio. Perhaps the elements could be divided into classes based on their oxide formulas. This procedure worked well with many elements. BeO, MgO, and CaO would form a group and so would B_2O_3, Al_2O_3, and Cr_2O_3. However, at this stage in the development of chemistry, there were too many confusing facts for chemists to proceed with this scheme. For example, the element iron forms several oxides — FeO, Fe_2O_3, and Fe_3O_4. Where would iron be placed in the oxide grouping? Another example is even more troublesome. Na_2O, K_2O, H_2O, and Cl_2O have the same type of formula. But in many other ways, these compounds are very different. Therefore, it is not reasonable to group the elements Na, K, H, and Cl together. It took chemists many years to unscramble some of these perplexing problems.

7-1 The Periodic Table

Dalton proposed in his Atomic Theory that the atoms of an element would have a characteristic mass. It was natural that chemists began to think of arranging the elements in the order of their molar masses. A number of the suggested arrangements were similar to the lost child's statement "cylindrical objects burn." Slowly, additional observations and more precise measurements resulted in an arrangement of the elements by the Russian chemist, Mendeleev. This proposal is summarized in the Periodic Table of the elements. This generalization was used by Mendeleev to predict that new elements with molar mass near the values 44, 68, and 72 grams would be discovered. In addition, he even predicted the properties of these elements and of their compounds. Table 7-3 compares Mendeleev's predictions with the observed properties for scandium, gallium, and germanium.

TABLE 7-3

Properties of the Elements
Scandium, Gallium, and Germanium

Property	Mendeleev's Predictions in 1871	Observed Properties
	Scandium (Discovered in 1877)	
Molar mass	44 g	43.7 g
Oxide formula	M_2O_3	Sc_2O_3
Density of oxide	3.5 g/ml	3.86 g/ml
Solubility of oxide	Dissolves in acids	Dissolves in acids
	Gallium (Discovered in 1875)	
Molar mass	68 g	69.4 g
Density of metal	6.0 g/ml	5.96 g/ml
Melting temperature	Low	30°C
Oxide formula	M_2O_3	Ga_2O_3
Solubility of oxide	Dissolves in ammonia solution	Dissolves in ammonia solution
	Germanium (Discovered in 1886)	
Molar mass	72 g	71.9 g
Density of metal	5.5 g/ml	5.47 g/ml
Color of metal	Dark gray	Grayish white
Melting temperature of metal	High	900°C
Oxide formula	MO_2	GeO_2
Density of oxide	4.7 g/ml	4.70 g/ml
Chloride formula	MCl_4	$GeCl_4$
Density of chloride	1.9 g/ml	1.89 g/ml
Boiling temperature of chloride	Below 100°C	86°C

We can duplicate the line of reasoning that led Mendeleev to his Periodic Table. However, we will also make use of the experimental information about the elements that is available to chemists today. Let us start by making a column of the elements, in order of increasing mass. A number of properties are placed beside each element in Table 7-4. The experimentally determined formulas for the

TABLE 7-4

Some Information About the First 21 Elements

Symbol for Element	Molar Mass, Grams	Numerical Order	Physical State at 25°C, 1 atm	Formula for Hydride	Formula for Fluoride	Formula for Oxide	Ionization Energy [kcal/mole]
H	1.01	1	gas	H_2	HF	H_2O	313.6
He	4.00	2	gas	–	–	–	567
Li	6.94	3	solid	LiH	LiF	Li_2O	124
Be	9.01	4	solid	BeH_2	BeF_2	BeO	215
B	10.8	5	solid	B_2H_6	BF_3	B_2O_3	191
C	12.0	6	solid	CH_4	CF_4	CO_2	260
N	14.0	7	gas	NH_3	NF_3	N_2O_5	335
O	16.0	8	gas	H_2O	OF_2	O_2	314
F	19.0	9	gas	HF	F_2	OF_2	402
Ne	20.2	10	gas	–	–	–	497
Na	23.0	11	solid	NaH	NaF	Na_2O	119
Mg	24.3	12	solid	MgH_2	MgF_2	MgO	176
Al	27.0	13	solid	Al_2H_6	AlF_3	Al_2O_3	138
Si	28.1	14	solid	SiH_4	SiF_4	SiO_2	188
P	31.0	15	solid	PH_3	PF_3	P_2O_5	254
S	32.1	16	solid	H_2S	SF_2	SO_3	239
Cl	35.5	17	gas	HCl	ClF	Cl_2O	300
Ar	39.9	18	gas	–	–	–	363
K	39.1	19	solid	KH	KF	K_2O	100
Ca	40.1	20	solid	CaH_2	CaF_2	CaO	141
Sc	45.0	21	solid	not known	ScF_3	Sc_2O_3	151

hydride, fluoride, and oxide are given for each element. Perhaps the first thing in this table that catches our eye concerns the elements He, Ne, and Ar. They are the only elements in our table that do not form oxides, hydrides, and fluorides. The next thing we notice is the repetition of formula types. When we reach Na, the set of chemical formulas is very much like the set for Li. The next element, Mg, has a set of chemical formulas like the set for Be. We can regroup these elements, starting with Na, placing each element directly below the element having similar formulas. The arrangement is shown in Table 7-5. The formula for the fluoride of each element is shown to help you recognize the similarity for each vertical group of elements.

TABLE 7-5

Periodic Groups
for the Elements Helium to Scandium

							He 2 —
Li 3 LiF	Be 4 BeF_2	B 5 BF_3	C 6 CF_4	N 7 NF_3	O 8 OF_2	F 9 F_2	Ne 10 —
Na 11 NaF	Mg 12 MgF_2	Al 13 AlF_3	Si 14 SiF_4	P 15 PF_3	S 16 SF_2	Cl 17 ClF	Ar 18 —
K 19 KF	Ca 20 CaF_2	Sc 21 ScF_3					

Chemical formulas and chemical properties across a row are very different as we move from one element to the next. On the other hand, formulas and properties of the elements in any vertical column are very similar. These vertical groups are called **chemical families** to emphasize similarities of the elements in each column.

You may be wondering why the first element, hydrogen, has been left out of our second arrangement of the elements. Compare the formulas H_2O and HF with the formulas Li_2O and LiF. The similarity in chemical formulas suggests that hydrogen should be in the same family with lithium. But now compare the formulas OH_2 and H_2 with formulas OF_2 and F_2. Perhaps hydrogen should be in the same family with fluorine. Chemists recognize that hydrogen is an unusual element. Some of its chemical properties indicate hydrogen should be placed with lithium. Other properties call for hydrogen to be grouped with fluorine. The problem is solved in the complete Periodic Table presented in Figure 7-1, by giving the element hydrogen a separate box.

In the last column of Table 7-4, the ionization energy for each element is given. The **ionization energy** is the amount of energy for the reaction

$$M(g) + \text{Ionization Energy} \longrightarrow M^{+}(g) + e^{-}$$

All elements undergo ionization to form a positive ion if enough energy is supplied. Values for the first ionization energy are plotted in Figure 7-2. As you can readily see, the ionization energy increases and decreases in a regular fashion as we proceed from one element to the next.

We shall now examine some of the important chemical families in detail.

PERIODIC TABLE

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 Ac-Lw	104 (260)	105													

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (248)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

FIGURE 7-1

The Periodic Table.

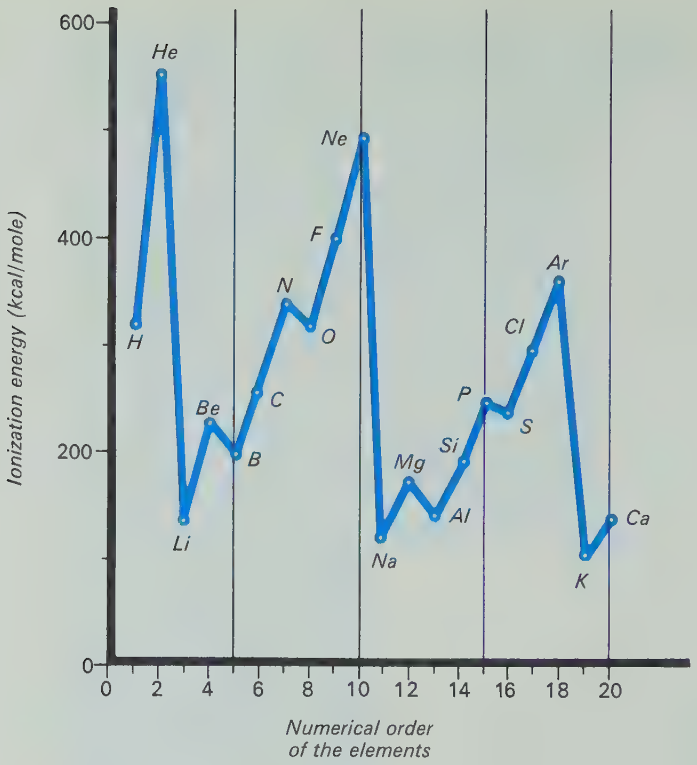


FIGURE 7-2

The relation between ionization energy and numerical order of the elements.

7-2 The Noble Gases

Almost two centuries ago, an English scientist, Cavendish, tried to convert atmospheric nitrogen into nitric oxides. There was always a small amount of gas that would not react. He was not able to explain this result. When these experiments were repeated in 1894, other scientists found the same result. No matter what chemical tests were tried, some of the gas would not enter any chemical reactions. It was concluded that a new element had been discovered. It was given the name *argon* from the Greek word meaning lazy. Additional careful experiments led to the isolation of four other gases from the atmosphere. The names *helium, neon, krypton,* and *xenon* were given to these elements. If you look back to Table 6-1, page 83, you can see that with the exception of argon, the amount of each noble gas in the atmosphere is very small.

It is interesting to realize that almost thirty years earlier, helium had been identified in the sun's atmosphere. When any substance is heated to a high enough temperature, light is emitted that is characteristic of the elements in the substance. During an eclipse of the sun in 1868, light in the sun's corona was observed that did not match any known element. On this basis a new element, called *helium,* was proposed in 1871. The noble gas elements precede each of the elements lithium, sodium, potassium, rubidium, and cesium. As we shall see in the next chapters, the noble gases supply an important key to understanding atomic structure. It is a curious quirk of nature that these gases are so important in the organization of our chemical knowledge. Of all the elements, the noble gases are the least reactive chemically. Until the last few years it was thought that the noble gases formed no chemical compounds.

Some of the properties of the noble gases are given in Table 7-6. Each of these elements exists as a monatomic gas at room temperature.

TABLE 7-6

Some Properties of the Noble Gases

Property	He	Ne	Ar	Kr	Xe	Rn
Position in numerical order	2	10	18	36	54	86
Molar mass of atoms, grams	4.00	20.0	39.9	83.7	131	222
Boiling temperature, °K	4.2	27.2	87.3	120	165	211
Melting temperature, °K	–	24.6	83.9	116	161	202
Ionization energy, kcal/mole	567	497	363	323	280	248

Boiling Temperatures

As a chemical family, the noble gases have the lowest boiling temperatures known. The values are shown in Figure 7-3. Helium has the lowest boiling temperature of any substance, 4.2°K. Neon, argon, krypton, xenon, and radon have successively higher boiling temperatures. Apparently as molar mass increases, the boiling temperature increases. We interpret a higher boiling temperature to mean that more energy must be supplied to allow a molecule to leave the liquid state.

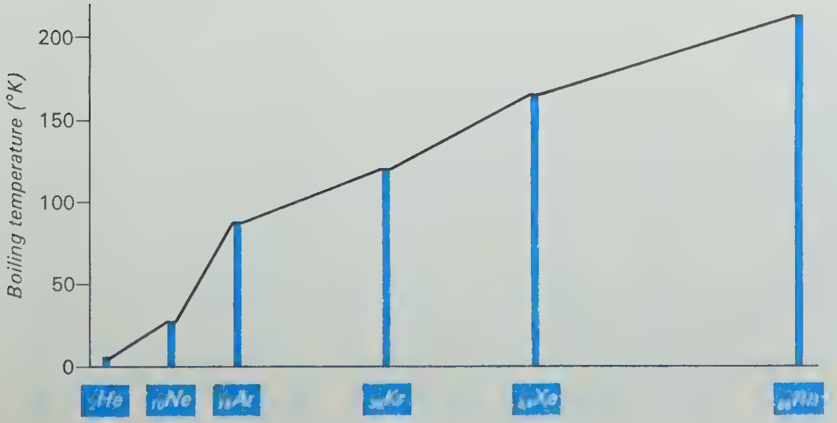


FIGURE 7-3

Trend in boiling temperature for the noble gases.

Melting Temperatures

We can see a regular variation in the melting temperatures for the noble gases. These unusual elements form solids at temperatures only slightly below the temperatures at which they boil. The small temperature range in which these elements exist as liquids suggests that the forces holding the solids together are very much like the forces in the liquids. The forces between noble gas molecules in the liquid or the solid are quite small. The melting temperatures for the noble gases are shown in Figure 7-4. No melting temperature for helium is listed in Table 7-6. Helium is the only substance, at one atmosphere pressure, that does not form a solid at any temperature. Helium becomes a solid at 1.1°K, at a pressure of 26 atmospheres. This fact indicates that the forces between helium molecules must be very weak.

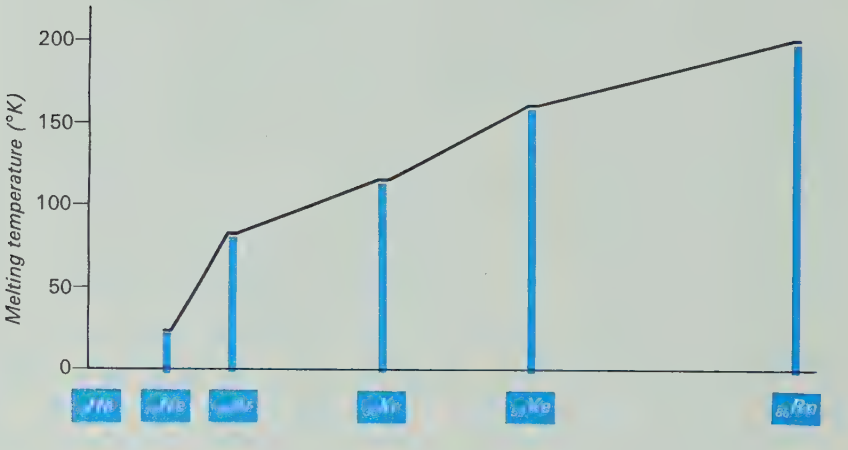


FIGURE 7-4

Trend in melting temperature for the noble gases.

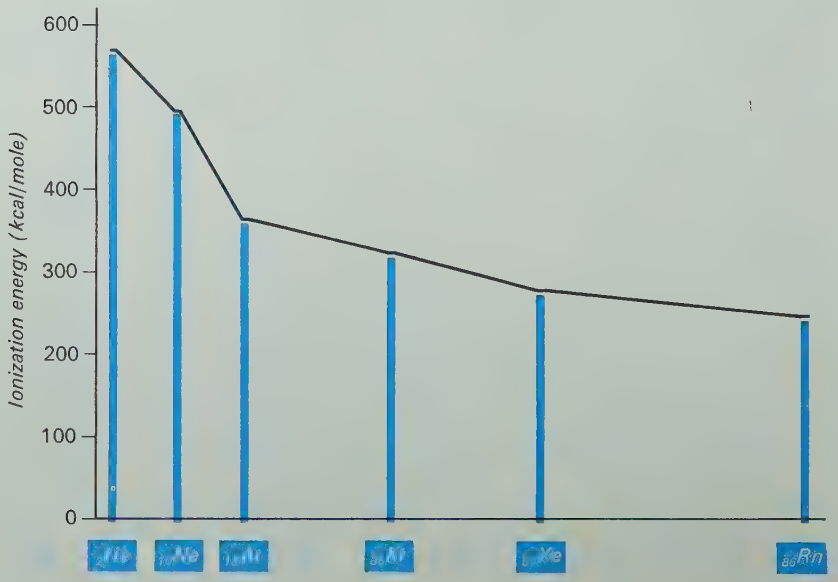


FIGURE 7-5

Trend in ionization energy for the noble gases.

Ionization Energy

The last property in Table 7-6 is the energy needed to ionize a mole of each noble gas. These energies form an important regularity. For the noble gases there is a decrease in ionization energy as we go from helium to neon to the others. These values are plotted in Figure 7-5. As we shall see, within any row in the Periodic Table, the ionization energy is highest for the noble gas element. The very stable atomic structures for these elements are indicated by the high ionization energies.

Chemical Properties

Another unique property of the noble gases lies in their very low chemical reactivity. This fact will be an important clue for us when we discuss atomic structure in Chapter 9. No compounds of these elements were known until 1962. The few compounds that have been prepared are extremely reactive. These compounds decompose readily to give the noble gas as one of the products. Some of the compounds are described in Table 7-7.

TABLE 7-7

Some Noble Gas Compounds

Compound	Form	Melting Temperature °C	Properties
XeF_2	colorless crystals	140	Reacts with H_2O to form Xe and O_2
XeF_4	colorless crystals	114	Stable
XeF_6	colorless crystals	48	Stable
XeO_3	colorless crystals	—	Explosive; stable in aqueous solution
KrF_2	colorless crystals	sublimes below 0°C	Decomposes spontaneously at room temperature

Everything that is known about the noble gases indicates that they have particularly stable atomic structures.

We turn now to the two chemical families that appear in the Periodic Table on either side of the noble gas family. In these two families we can see some of the regularities in chemical and physical properties that make the Periodic Table so valuable to chemists.

7-3 The Alkali Elements

The **alkali elements** lithium, sodium, potassium, rubidium, cesium, and francium occupy a position in the numerical order of the elements immediately following a noble gas. These elements are metallic solids at 25°C. When the surfaces are clean, the alkali metals have a bright, silvery appearance. Exposure to air causes the surfaces to tarnish rapidly. The metals are excellent conductors of heat and electricity. The alkali metals have very high chemical reactivity. Some of their properties are listed in Table 7-8. Francium is not included since it is a very rare element.

TABLE 7-8

Some Properties of the Alkali Metals

Property	Li	Na	K	Rb	Cs
Position in numerical order	3	11	19	37	55
Molar mass of atoms, grams	6.94	23.0	39.1	85.4	133
Boiling temperature, °C	1326	889	757	679	690
Melting temperature, °C	180	98	63	39	29
Density at 20°C, g/ml	0.54	0.97	0.86	1.53	1.90
Ionization energy, kcal/mole	124	119	100	96	90

Boiling and Melting Temperatures

The alkali metals are solids at room temperature. Cesium, however, melts at a few degrees above room temperature. Both melting and boiling temperatures decrease as the molar masses increase. The opposite trend is found for the noble gases. Figure 7-6 contrasts the trends for these two families. Notice also the wide temperature range over which the alkali elements are liquids. Sodium, for instance, melts at 98°C and boils at 889°C, almost 800° higher. Contrast this with neon which boils 2.6° higher than it melts. How different are the alkali elements from the noble gases!

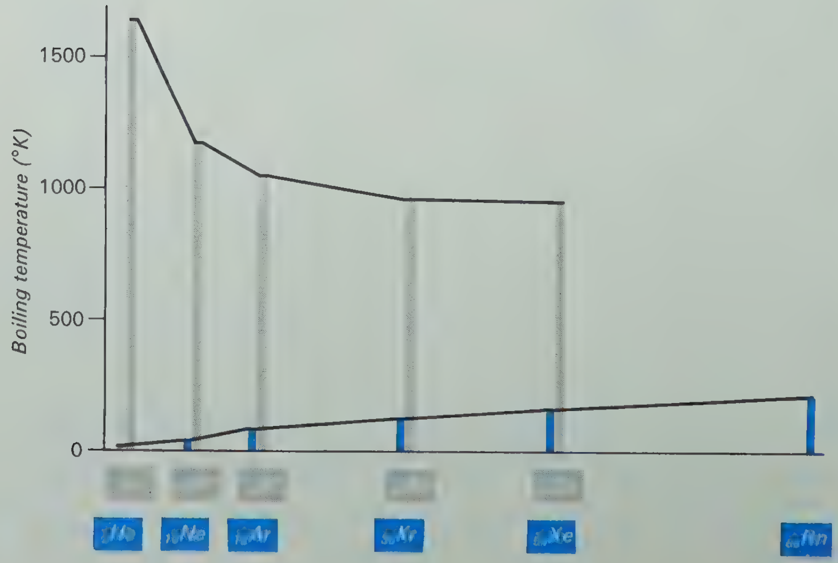


FIGURE 7-6A

Comparison of boiling temperatures for the noble gases and the alkali metals.

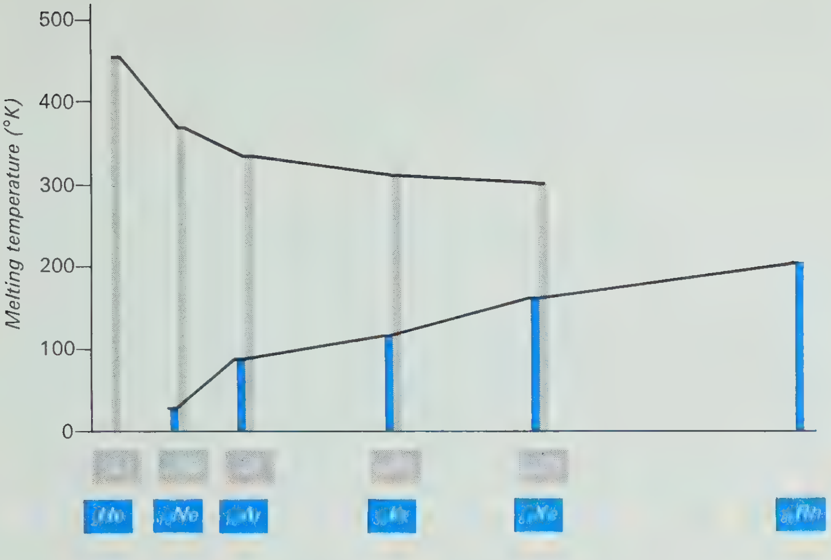


FIGURE 7-6B

Comparison of melting temperatures for the alkali metals and the noble gases.

Ionization Energy

Very little energy is required to ionize the alkali elements. Again we see a great difference between the noble gases and the alkali metals. Figure 7-7 contrasts the ionization energies for these two chemical families. For each family the ionization energy decreases as the order number increases.

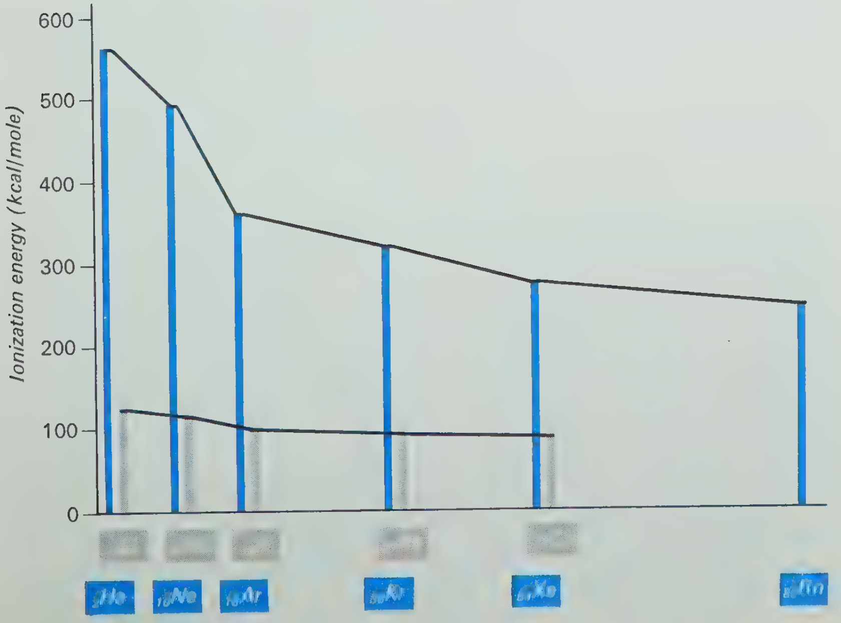


FIGURE 7-7

Comparison of ionization energies for the alkali metals and the noble gases.

Chemical Properties of the Alkali Metals

The alkali metals have high chemical reactivity. They react vigorously with oxygen, chlorine, or water. It will be interesting to investigate some of these reactions.

When chlorine gas is brought in contact with hot sodium metal, solid sodium chloride is formed.

$$2\ \mathrm{Na}(l) + \mathrm{Cl_2(g)} \longrightarrow 2\ \mathrm{NaCl(s)} + \text{energy}$$

We have seen in Chapter 6, page 94, that solid NaCl has a regular arrangement of sodium ions, Na^+, and chloride ions, Cl^-, in the crystal. In the reaction between sodium and chlorine, ions are formed. The ions attract each other because they have opposite electric charge. The stability of the sodium chloride crystal depends on the electrical attraction of oppositely charged ions. The crystal is held together by **ionic bonds.** This chemical behavior is characteristic of all the alkali metals. Each alkali metal reacts with chlorine gas in a similar way. Ionic solids, which are soluble in water, form in these reactions.

EXERCISE 7-1

Write the four equations for the reactions between chlorine and lithium, potassium, rubidium, and cesium.

Reaction of the Alkali Metals with Water

Sodium metal reacts with water to form hydrogen gas and an aqueous solution of sodium hydroxide, NaOH.

$$2\ \mathrm{Na(s)} + 2\ \mathrm{H_2O} \longrightarrow 2\ \mathrm{Na^+(aq)} + 2\ \mathrm{OH^-(aq)} + \mathrm{H_2(g)} + \text{energy}$$

Energy is liberated. The reaction often takes place so rapidly that the temperature rises and the hydrogen, mixing with air, explodes. Sodium metal is dangerous and must be handled with caution. Sodium is usually stored in oil so that moisture in air does not come in contact with the metal.

All of the alkali metals react with water in a similar way. The reaction becomes more vigorous as we examine each metal from lithium to cesium. Two ions are formed in each reaction. The first is an alkali element ion with a charge of 1+. The other ion, $OH^-(aq)$, is called the **hydroxide ion.** The properties of basic solutions are attributed to this ion. We shall come across this ion again in Chapter 14.

EXERCISE 7-2

Write the four equations for the reactions between water and lithium, potassium, rubidium, and cesium.

7-4 The Halogens

If we move across the Periodic Table, we find a family of elements called the **halogens.** They have the names *fluorine, chlorine, bromine, iodine,* and *astatine.* Astatine is a very rare element. It will not be part of our discussion.

Some of the physical properties of the halogens are given in Table 7-9. In the elemental state, the halogens form stable diatomic molecules. At very high temperatures these diatomic molecules break down to form atoms. For example, it is known that chlorine near the surface of the sun is present as single chlorine atoms. At lower temperatures, chlorine atoms react with each other to form molecules.

$$2\,\text{Cl(g)} \longrightarrow \text{Cl}_2\text{(g)} + \text{energy}$$

TABLE 7-9

Some Properties of the Halogens

Property	Fluorine	Chlorine	Bromine	Iodine
Position in numerical order	9	17	35	53
Molar mass of atoms, grams	19.0	35.5	79.9	127
Molecular formula at 25°C	F_2	Cl_2	Br_2	I_2
Boiling temperature				
°K	85	238.9	331.8	457
°C	−188	−34.1	58.8	184
Melting temperature				
°K	55	172	265.7	387
°C	−218	−101	−7.3	114
Color	Pale yellow	Yellow green	Red	Black (purple vapor)
State at 25°C	gas	gas	liquid	solid
Ionization energy, kcal/mole	402	300	273	241

Boiling and Melting Temperatures

We have already compared the boiling and melting temperatures for the noble gases and the alkali metals. When we look at those temperatures for the halogens in Figure 7-8, there seems to be some similarity with noble gases. The melting and boiling temperatures of the halogens increase as the molar masses increase. This trend suggests that forces between halogen molecules in the liquid and solid states are the weak variety that account for the liquefaction of the noble gases.

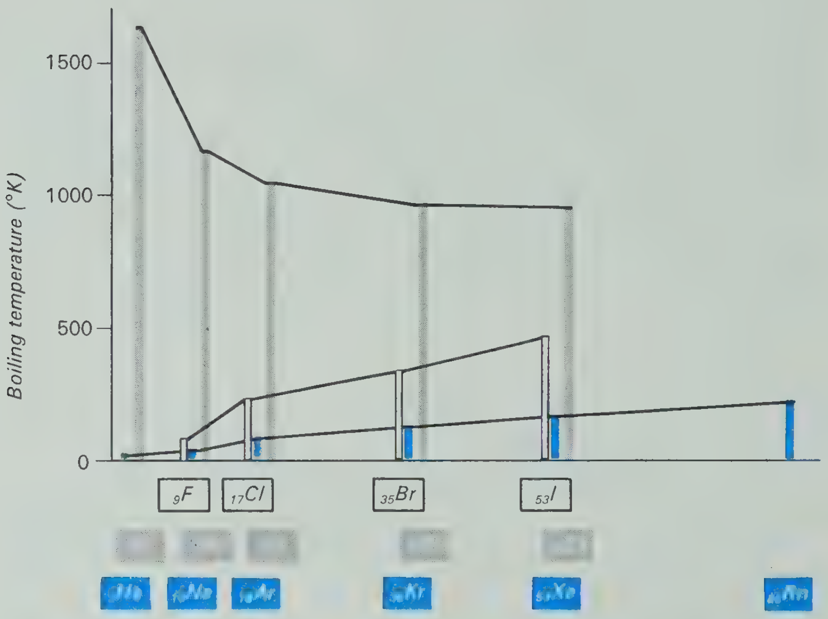
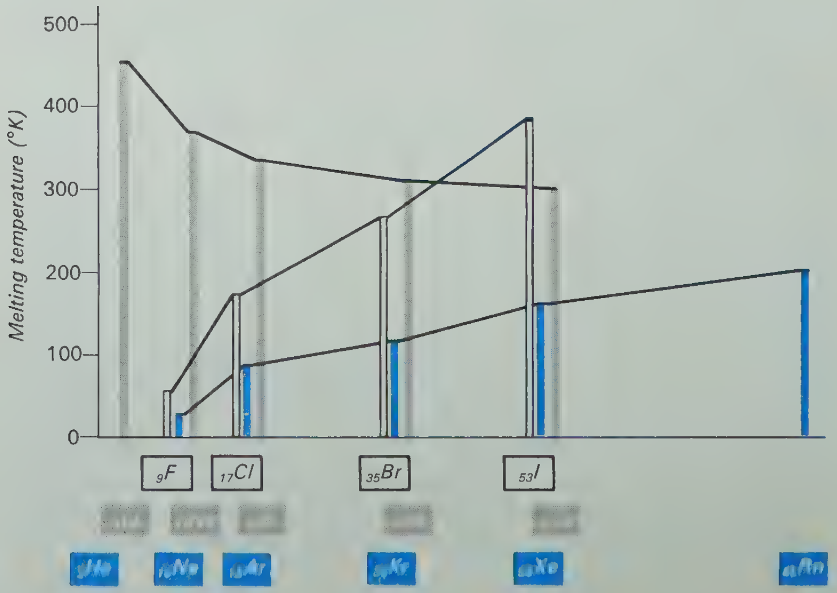


FIGURE 7-8

A. Boiling temperatures for the halogens, the alkali metals, and the noble gases.



B. Comparison of melting temperatures for the halogens, the alkali metals, and the noble gases.

The ionization energies for the halogens decrease as we go from fluorine to iodine. We have noticed this trend for the noble gases and for the alkali metals. Numerically, the ionization energies for the halogens are almost as large as the values for the noble gases. This fact indicates that it is difficult to remove an electron from the halogens. Figure 7-9 contrasts the ionization energies for the three families we have discussed in this chapter.

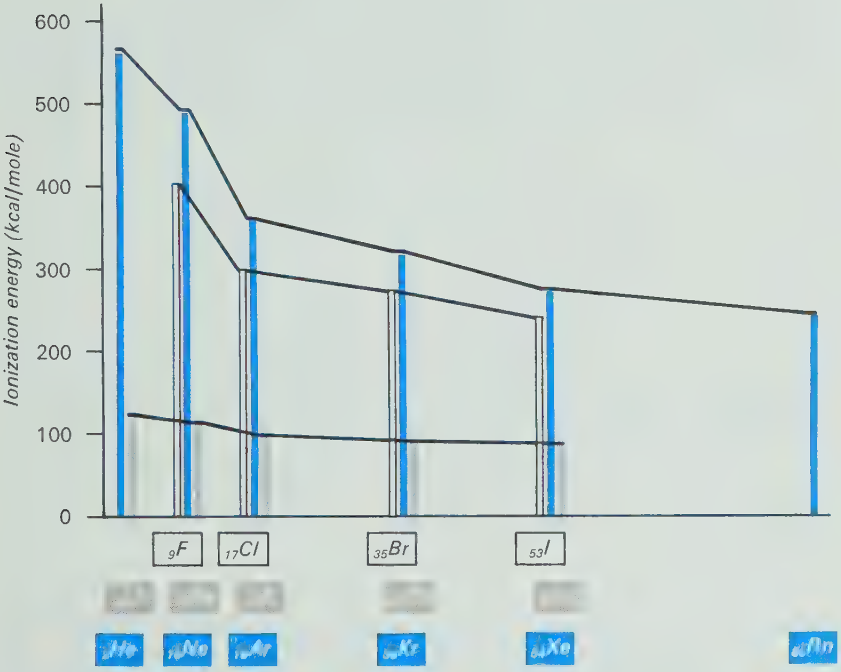


FIGURE 7-9

Comparison of ionization energies for the halogens, the alkali metals, and the noble gases.

The Chemistry of the Halogens

The reactions of the halogens with one of the alkali metals show similarity within this family.

$$2\,K(s) + F_2(g) \longrightarrow 2\,KF(s) + \text{energy}$$
$$2\,K(s) + Cl_2(g) \longrightarrow 2\,KCl(s) + \text{energy}$$
$$2\,K(s) + Br_2(g) \longrightarrow 2\,KBr(s) + \text{energy}$$
$$2\,K(s) + I_2(g) \longrightarrow 2\,KI(s) + \text{energy}$$

These reactions proceed readily. Ionic solids, with the general formula KX, are formed. Each of these white solids is crystalline, with the same structure that we saw for NaCl, page 94. The negative ions F^-, Cl^-, Br^-, and I^- are called **halide ions.**

EXERCISE 7-3

Write the equations for the reactions between each alkali metal and the halogen which is in the same row of the Periodic Table.

The halogens react with hydrogen gas to form the hydrogen halides.

$$H_2(g) + F_2(g) \longrightarrow 2\,HF(g) + \text{energy}$$
$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) + \text{energy}$$
$$H_2(g) + Br_2(g) \longrightarrow 2\,HBr(g) + \text{energy}$$
$$H_2(g) + I_2(g) \longrightarrow 2\,HI(g) + \text{energy}$$

The hydrogen halides are gases at room temperature. The most important properties of the hydrogen halides are seen in their aqueous solutions. These compounds are very soluble in water. They give solutions that conduct electric current. This property suggests that ions are present. The reactions can be written in this way.

$$HF(g) + \text{water} \longrightarrow H^+(aq) + F^-(aq)$$
$$HCl(g) + \text{water} \longrightarrow H^+(aq) + Cl^-(aq)$$
$$HBr(g) + \text{water} \longrightarrow H^+(aq) + Br^-(aq)$$
$$HI(g) + \text{water} \longrightarrow H^+(aq) + I^-(aq)$$

These solutions have similar properties and are called acid solutions. The common species in the solutions is the **aqueous hydrogen ion, $H^+(aq)$.** The properties of acid solutions are attributed to this ion. We shall discuss acids and bases more extensively in Chapter 14.

7-5 Review

The Periodic Table proposed by the Russian chemist, Mendeleev, is one of the most important regularities in chemistry. By arranging the elements as in the diagram shown inside the front cover of this book, we can simplify the problem of understanding and remembering the large number of experimental observations made by chemists.

The elements grouped in vertical columns have very similar properties. In this chapter, we have discussed three chemical families: the *noble gases,* the *alkali metals,* and the *halogens.* It is easy to see that general statements can be made about the chemical and physical properties of these elements and about the compounds they form. There will be many more examples in this book of the usefulness of the Periodic Table.

The search for an explanation of the periodic properties of the elements was a long one. The key was found to be an understanding of atomic structure, but this eluded scientists for many years. In the next two chapters we will outline the experiments and the interpretations that led to our present model of the atom.

Questions and Problems for Chapter 7

1

Write the molecular formulas of the hydrogen compounds of the second-row elements, Li, Be, B, C, N, O, F, Ne. Indicate, for each compound, the H/M atom ratio.

2

What is the significance of the trends in the boiling temperatures and melting temperatures of the noble gases in terms of attractions among the atoms?

3

Why is argon used in many electric light lamps?

4

Which of the following is NOT a correct formula for a substance at normal laboratory conditions?

(a) $H_2S(g)$
(b) $CaCl_2(s)$
(c) $He(g)$
(d) $NaNe(s)$
(e) $Al_2O_3(s)$

5

Use the information in Table 7-8, page 112, to prepare a column listing the properties of element 87, francium. Give balanced equations for some chemical reactions expected for francium.

6

Use the information in Table 7-9, page 115, to prepare a column listing the properties of element 85, astatine. List some chemical reactions expected for astatine.

7

How do the trends in physical properties for the halogens compare with those for the noble gases? Compare boiling temperatures, melting temperatures, and ionization energies.

8

Chlorine is commonly used as a germicide in swimming pools. When chlorine dissolves in water, it reacts to form hypochlorous acid,

$$Cl_2 + H_2O \rightleftharpoons HOCl(aq) + H^+(aq) + Cl^-(aq)$$

Predict what happens when bromine, Br_2, dissolves in water. Write the equation for the reaction.

9

From the following experimental information, identify which chemical family and which element is described. Answer each part separately.

Identify the specific element as soon as possible.

Element A:

(a) has an ionization energy of more than 400 kcal/mole.
(b) is a gas at room temperature.
(c) reacts readily with element number 11 to form an ionic solid.
(d) has the highest ionization energy of any element in the family.

Element B:

(a) has an ionization energy less than 400 kcal/mole.
(b) has a boiling temperature above 800°C.
(c) reacts with certain elements to form ionic solids.
(d) reacts with hydrogen in a one to one ratio.
(e) reacts with water to liberate hydrogen gas.
(f) has the lowest molar mass and density of any element in the family.

Element C:

(a) does not form a hydride.
(b) has a boiling temperature below 25°C.
(c) has an ionization energy less than 300 kcal/mole.
(d) forms compounds with both fluorine and oxygen.

10

Follow the instructions for Problem 9.

Element D:

(a) is a solid at room temperature.
(b) reacts with certain elements to form ionic solids.
(c) forms a hydride.
(d) does not react with water.

Element E:

(a) is a good conductor of electricity.
(b) melts at a temperature a few degrees above 25°C.
(c) has a low ionization energy.

Element F:

(a) readily forms a gaseous hydride.
(b) the hydride reacts with water to form an acidic solution.
(c) reacts with hot alkali metals to form an ionic solid.
(d) has the lowest boiling temperature and the highest ionization energy of any element in the family.

11

The metals of the second column of the Periodic Table combine with the halogens to form ionic solids. Write a general equation to represent these reactions using M for the metals and X for the halogens.

12

Use Table 7-4 and the Periodic Table to suggest formulas for compounds of the following pairs of elements.

(a) strontium-sulfur
(b) gallium-fluorine
(c) beryllium-tellurium
(d) chlorine-iodine
(e) arsenic-bromine

13

The metallic elements Na, Mg, and Si in row 3 of the Periodic Table have atomic radii of 1.9, 1.60, and 1.3 Å. Estimate the size of an aluminum atom in a metal sample.

14

The size of an atom can be expressed as the closest distance of approach by another atom. For the halogens the values are F, 1.35; Cl, 1.80; and Br, 1.95 Å. Estimate the value for iodine.

15

The heat of vaporization of some elements in row 5 of the Periodic Table are: Y, 94; Zr, 139; Mo, 142; Tc, 138; Rh, 118; and Ag, 61 kcal/mole. Estimate values for Nb, Pd, and Ru.

The Structure of the Atom

8

We have seen how chemists in the nineteenth century, looking for a way to arrange the elements, developed the Periodic Table. At the same time many physicists were carrying out experiments on the conduction of electricity in gases. In this chapter we will look at these experiments. They provided the clues that eventually led to our present model for atomic structure. Like the conclusion of a mystery story, the explanation now seems clear and simple.

Look carefully at the apparatus outlined in Figure 8-1. Metal electrodes are sealed in each end of a long glass tube. A vacuum pump for removing gas is attached to the glass tube. A high voltage, about 10,000 volts, can be applied to the electrodes. When the gas pressure in the tube is at one atmosphere, no electric current flows through the tube. When the gas pressure is decreased to about 0.01 atmosphere, an electric current flows. At the same time, light is emitted by the gas. You have seen this phenomenon many times. The neon lights used in advertising signs operate this way. These lights contain gas at low pressure.

As the gas pressure in the tube is decreased further, a sequence of observations can be made. A dark space appears in the vicinity of one electrode. This electrode is called the *cathode.* Alternate light and dark spaces can be seen between the two electrodes. This pattern is shown in Figure 8-1. At still lower gas pressures, about 10^{-6} atmosphere, the dark space increases in length until it reaches the other electrode. This electrode is called the *anode*. At such low pressures, no light is given out by the small amount of gas in the tube. Instead something new can be observed. The glass of the tube glows with a faint greenish light. We say that the glass fluoresces.

Some physicists carried out experiments to explore what happened inside the discharge tube. Other physicists were interested in studying the light emitted by the gas. To pick up the various

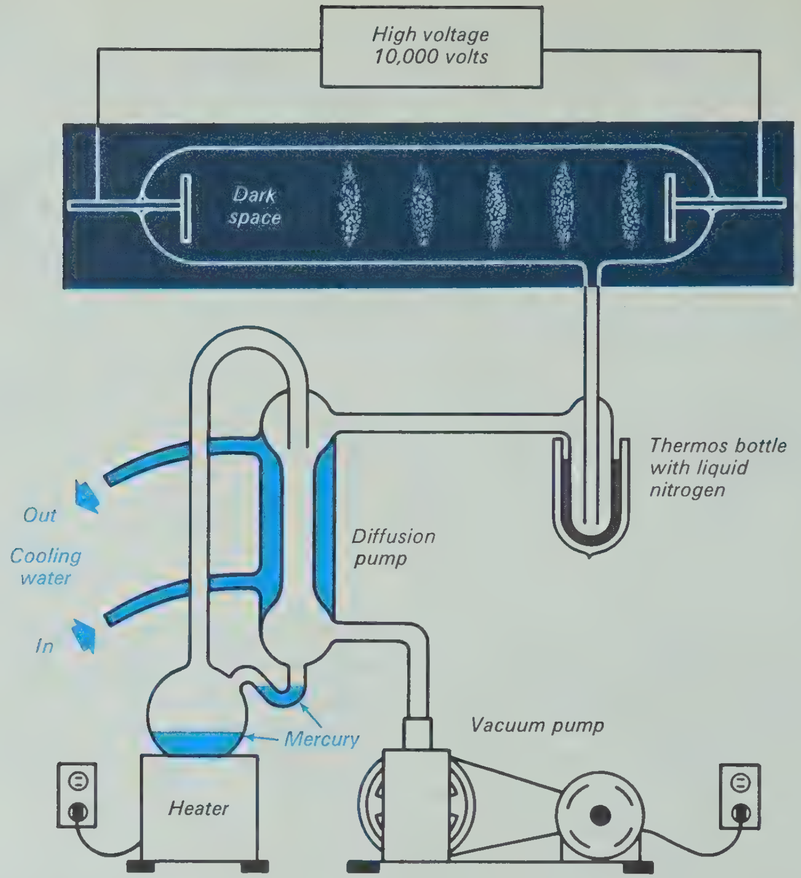

High voltage
10,000 volts
Dark space
Thermos bottle with liquid nitrogen
Out
Cooling water
In
Diffusion pump
Mercury
Vacuum pump
Heater

FIGURE 8-1

Gaseous discharge tube and vacuum system.

threads of the story, we will first discuss light and its energy. Then we will outline the experiments that led to the discovery of the electron.

8-1 Light

Many of you have used a small lens to focus sunlight on a piece of paper. With patience you can increase the temperature of the paper until it finally bursts into flame. A solar furnace develops a temperature of several thousand degrees by focusing sunlight. Almost any substance can be melted in such a furnace. The temperature rise means that energy has been absorbed. This energy must be carried by light. A study of the energy carried by light will help us understand additional experiments with gas discharge tubes.

Light is often described as a wave motion. Any wave motion can be discussed in terms of frequency and wavelength. We can understand these words by thinking of a familiar example of waves, waves in water. Suppose you were standing on a cliff looking out over the ocean. On most days, you could see waves that move toward the shore in regular fashion. You can watch these waves as they approach the beach. The noise of the breakers and the erosion of the beach demonstrate that water waves carry energy. The wave is a pulse of energy moving through the water. The energy of some distant disturbance, perhaps storm winds at sea or an earthquake, is carried through the ocean by water waves. Some of the energy is expended when the waves crash on the beach.

Suppose there is a small boat drifting far out on the ocean. You can see the boat rise and fall with each wave. However, the boat does not seem to move forward with the wave. The motion of the boat is up and down, at right angles to the motion of the energy pulse. We use the word *frequency* to tell how many times the boat rises on a wave every second. For water on the ocean, the frequency might be one wave every twenty seconds. The frequency would be $^1/_{20}$ or 5×10^{-2} wave per second. The Greek letter nu, ν, is used as shorthand for frequency of wave motion. Another word that is important when talking of wave motion is *wavelength.* Wavelength is the distance from the top of one wave to the top of the next wave. In the ocean the wavelength might be 50 feet. The Greek letter lambda, λ, is used as shorthand for wavelength.

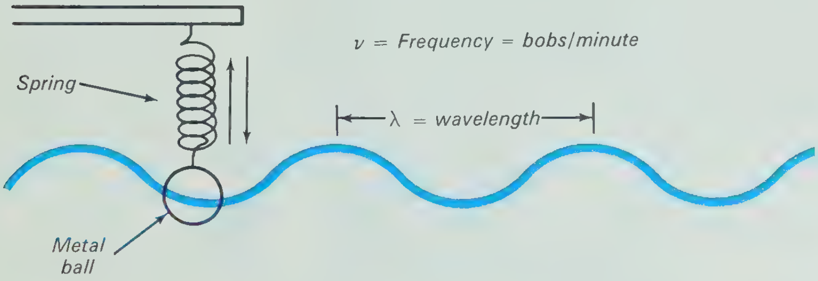


FIGURE 8-2

A mass on a spring, responding to water waves.

Light is a form of energy that can travel through space. For many experiments it is helpful to think of light as a wave motion. These waves can be described by their frequency and by their wavelength. An instrument called a *spectrograph* helps us learn more about light. A simple spectrograph is shown in Figure 8-3. A source of light is provided by a hot tungsten wire. The wire is heated by passing electric current through it. At about 1000°C the wire glows with a bright white light. Some of this light enters a narrow slit and is focused into a beam by the lens. The light beam, passing through the prism, is bent or refracted. The different frequencies that make up white light are bent through different angles and a rainbow of colors can be seen. Each color corresponds to a wave with a particular frequency and wavelength. After passing through the prism, the light can be focused on a photographic film. After the photographic film has been developed, it shows a broad darkened region. The pattern, recorded on the film, is called the **spectrum** of light. All colors of light from red to blue are present in the light from a hot tungsten wire. Such a spectrum is called a continuous spectrum. In Table 8-1 the frequencies and wavelengths for light waves are compared with values for water waves Red and blue light waves have very high frequencies. Their wavelengths are small.

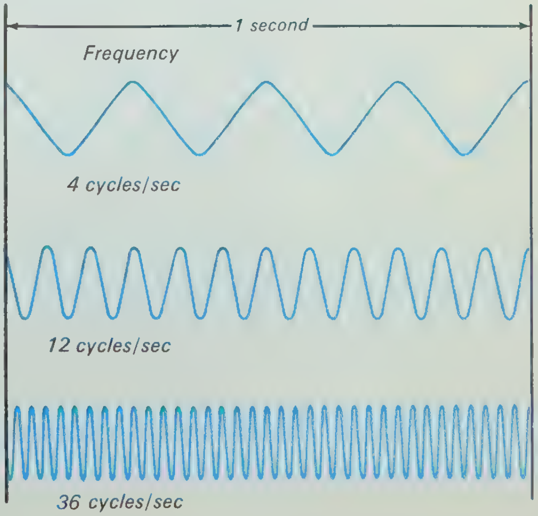


TABLE 8-1

Frequency and Wavelength for Different Kinds of Waves

Kind of Wave	Frequency (number per second)	Wavelength (centimeters)
Water	5×10^{-2}	1.5×10^{3}
Red light	4.3×10^{14}	7.0×10^{-5}
Blue light	7.5×10^{14}	4.0×10^{-5}

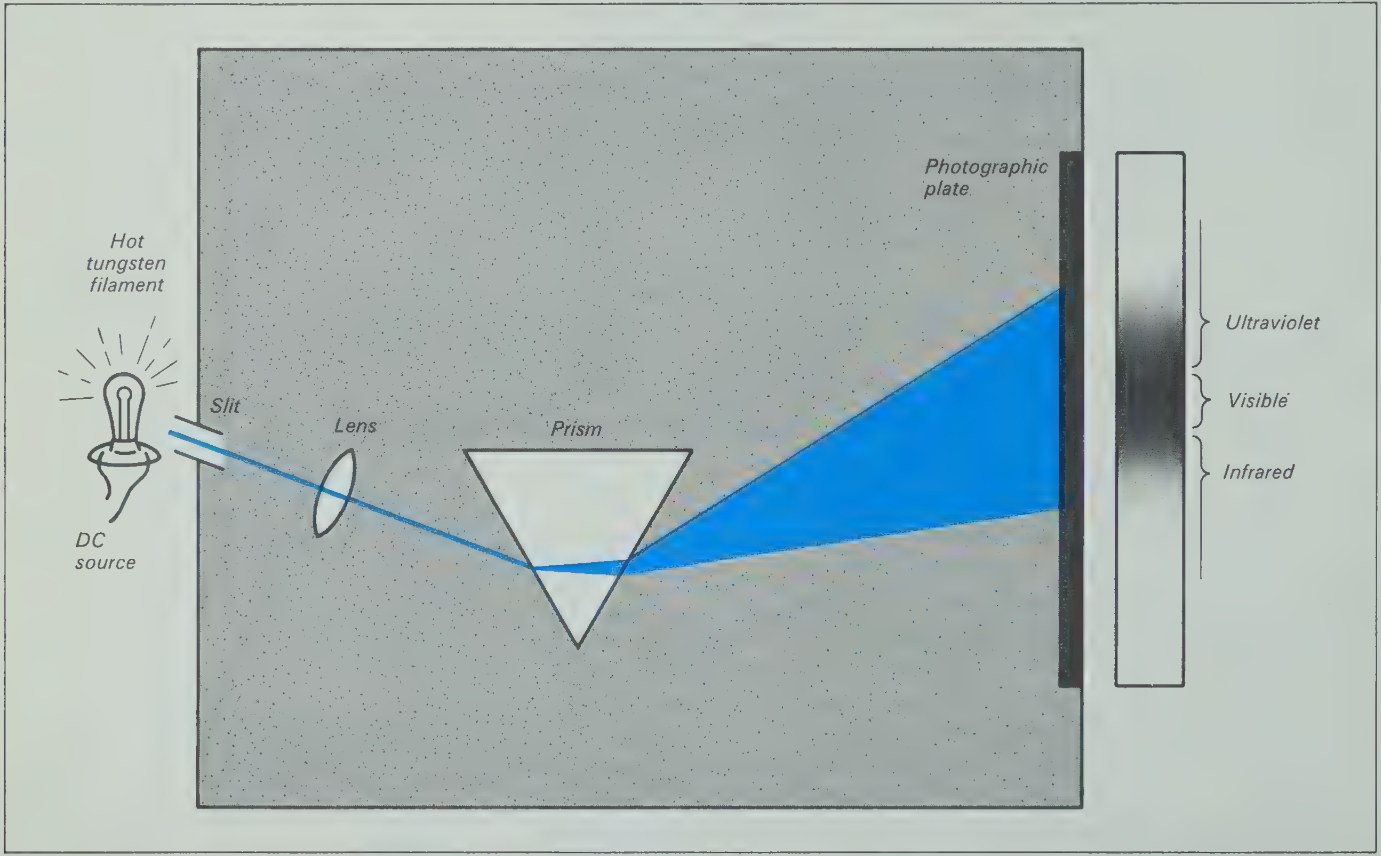


FIGURE 8-3 The continuous spectrum of light emitted by a hot tungsten wire.

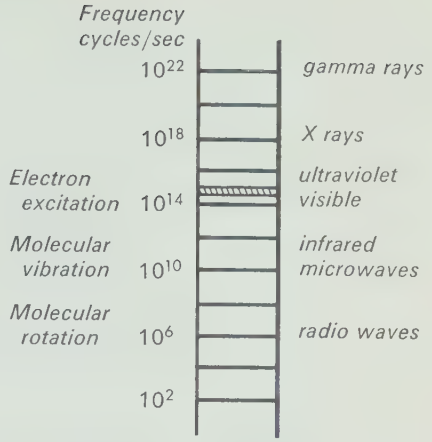
The darkening of the photographic film extends outside the familiar rainbow of colors. There are frequencies of light emitted by the hot tungsten wire that cannot be detected by the human eye. Light waves with frequencies somewhat lower than the frequency of red light are called **infrared rays.** Light waves with frequencies just higher than the frequency of blue light are called **ultraviolet rays.**

It is important to talk about energy in quantitative terms. How much energy is carried by light? The answer is simple in mathematical form but not simple in concept. We have already seen that matter occurs in units called atoms. Electric charge also comes in units. Energy in the form of light comes in units too. These units of energy are called **photons.** Each photon contains an amount of energy determined by the frequency of light. A German scientist, Max Planck, first proposed the equation relating energy and frequency.

$$E = h\nu$$

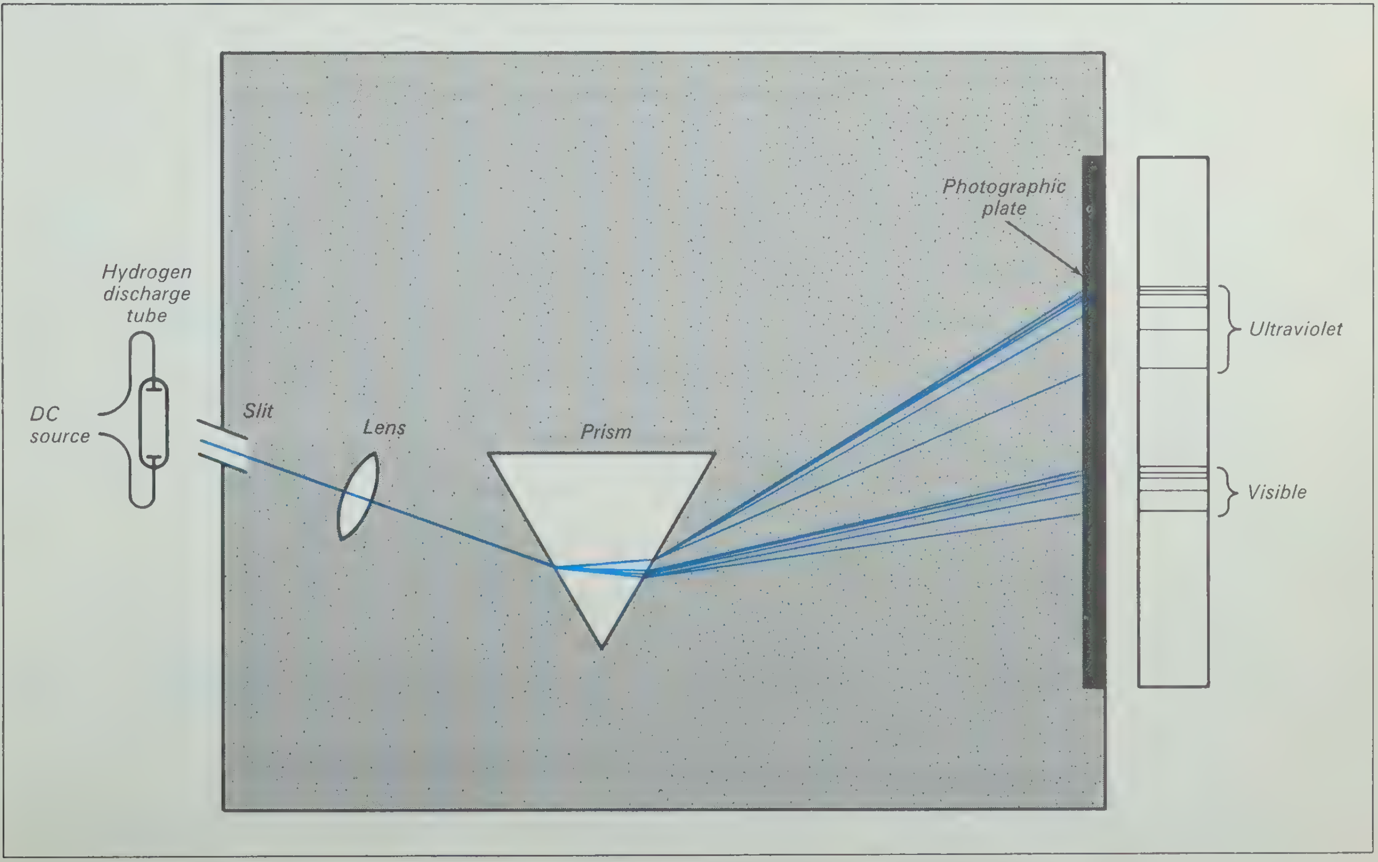
The quantity h is called Planck's constant. It is a conversion factor to change frequency units into energy units. The experimental evidence that led to this equation is a fascinating story. However, we will not discuss these experiments in this book. Perhaps you will hear about them in a physics class some day.

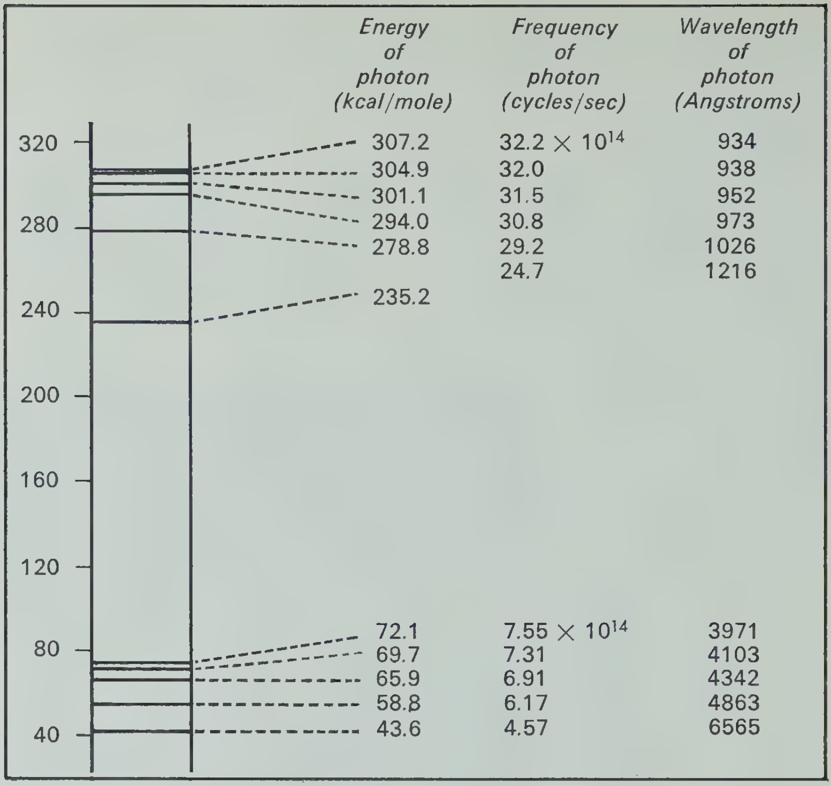
Let us look now at the experiment with the spectrograph shown in Figure 8-4. We have changed the light source. The tungsten wire is replaced by a discharge tube containing hydrogen gas at low pressure. When electric current flows in the hydrogen discharge tube, red light is emitted. Once again the spectrum from this light source is recorded on photographic film. The spectrum consists of a series of sharp lines. Each line corresponds to a particular frequency of light emitted by hydrogen atoms. Between these lines the film has not been darkened. One interpretation is that hydrogen emits light at certain frequencies only. This kind of spectrum is called a **line spectrum.** All elements in the gas phase emit characteristic


Frequency cycles/sec
10^{22}
10^{18}
10^{14}
10^{10}
10^{6}
10^{2}
gamma rays
X rays
ultraviolet
visible
infrared
microwaves
radio waves
Electron excitation
Molecular vibration
Molecular rotation

The electromagnetic energy spectrum.

FIGURE 8-4 The line spectrum of light emitted by a hydrogen discharge tube.


Hydrogen discharge tube
DC source
Slit
Lens
Prism
Photographic plate
Ultraviolet
Visible


Energy of photon (kcal/mole)
Frequency of photon (cycles/sec)
Wavelength of photon (Angstroms)
320
280
240
200
160
120
80
40
307.2 32.2 × 10^14 934
304.9 32.0 938
301.1 31.5 952
294.0 30.8 973
278.8 29.2 1026
24.7 1216
235.2
72.1 7.55 × 10^14 3971
69.7 7.31 4103
65.9 6.91 4342
58.8 6.17 4863
43.6 4.57 6565

The line spectrum of the hydrogen atom, in the visible and ultraviolet regions.

line spectra when they are heated to a high temperature or when an electric discharge passes through them. Most line spectra of the elements are complex, containing many separate lines. Only a few elements have line spectra that are simple.

Because of its simplicity the pattern exhibited in the hydrogen spectrum intrigued scientists. Did the spectrum of hydrogen depend on the structure of the hydrogen atom? Many scientists thought this was a reasonable assumption. An explanation for the line spectrum of hydrogen might lead to an understanding of the atomic structure for hydrogen. But the search for an explanation was a long one.

In 1885 Balmer proposed a simple mathematical relation for the frequencies in the visible portion of the hydrogen spectrum.

$$\nu = 3.29 \times 10^{15}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3, 4, 5 \ldots$$

The different frequencies of the spectral lines are obtained by changing n from 3 to 4 to 5 and so on. As an example, let $n = 3$.

$$\nu = 3.29 \times 10^{15}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 4.57 \times 10^{14} \text{ waves per second}$$

This frequency corresponds to the first line in the visible part of the hydrogen spectrum.

EXERCISE 8-1

Draw a line 8 cm long on a piece of paper and mark off 2 cm divisions. Label each of these divisions from 4.0×10^{14} to 8.0×10^{14} waves per second. Use the Balmer formula to calculate ν when $n = 4, 5, 6, 7,$ and 8. Draw a vertical mark for each of these frequencies on your frequency scale. Include the value for $n = 3$ calculated in the example above.

This formula is in agreement with the experimental fact that the spectral lines get closer and closer together as one moves toward the blue end of the spectrum. The agreement between the frequencies calculated from this simple formula and the experimental spectral lines was amazing. Scientists were convinced that some simple model for the hydrogen atom would provide an explanation for the spectrum and for the Balmer formula. It was almost thirty years later, after many more experiments, that a suitable model was proposed.

8-2 The Discovery of the Electron

Now return to the gas discharge tube we discussed earlier. At sufficiently low pressures the glass of the discharge tube glows with a greenish light when electricity passes through the gas. A perforated shield is placed in the tube to form a narrow beam of cathode rays. A fluorescent screen lets us follow the movement of the beam. The experiment illustrated in Figure 8-5 provides a very important

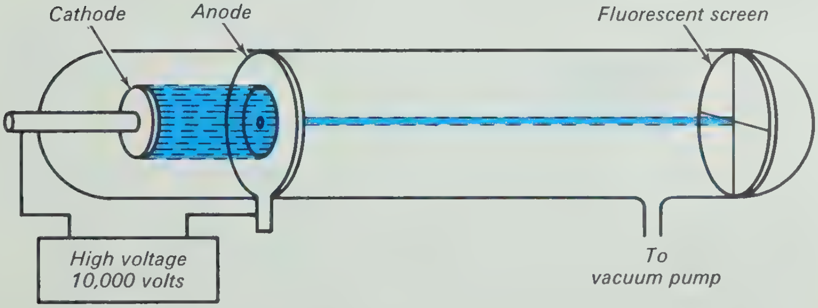


FIGURE 8-5

Gaseous discharge tube. Cathode rays pass through hole in anode. Size and position of spot on screen suggest cathode rays travel in straight lines.

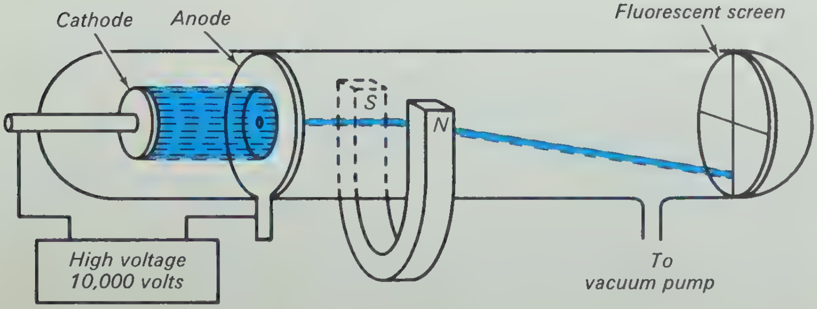


FIGURE 8-6

Gaseous discharge tube. Cathode rays deflected in magnetic field in same direction that negative electric charge is deflected.

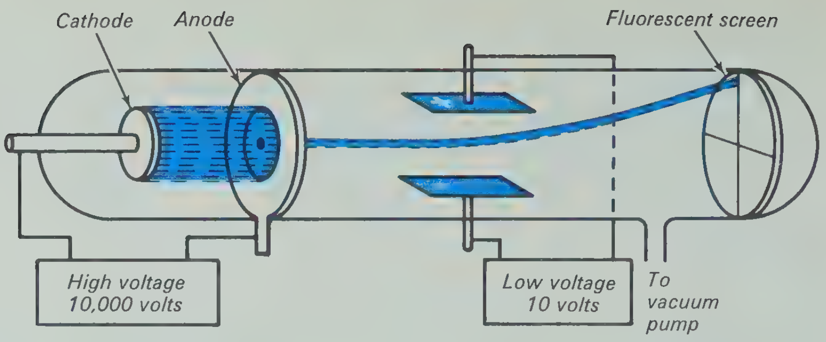


FIGURE 8-7

Gaseous discharge tube. Cathode rays deflected in electric field in same direction that negative electric charge is deflected.

fact. *Something comes from the cathode.* The size of the spot on the fluorescent screen compared to the size of the hole in the anode indicates that these "cathode rays" travel in straight lines. Additional experiments showed that cathode rays carry negative electric charge. These experiments are illustrated in Figures 8-6 and 8-7. When a magnet is placed near the tube, the cathode rays are deflected. This behavior is like the behavior of negatively charged particles. The direction of deflection suggests that the cathode rays carry a negative electric charge. Figure 8-7 shows the same apparatus with two additional electrodes sealed in the discharge tube. An electrical voltage can be applied to these electrodes. The cathode rays move toward the positively charged electrode. This result also indicates that cathode rays carry negative electric charge.

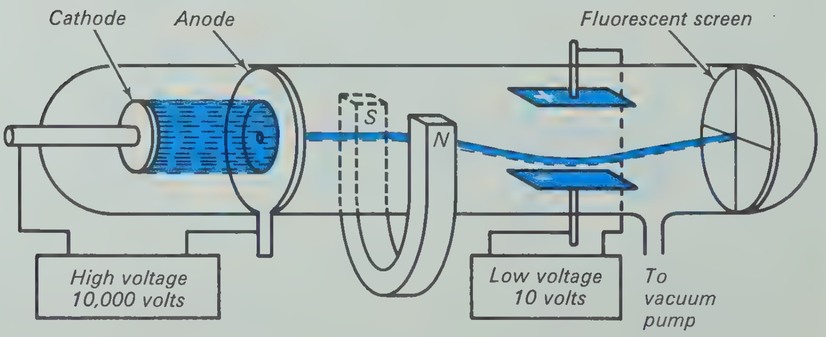


FIGURE 8-8

Gaseous discharge tube set up for the *e*/*m* experiment. Cathode rays deflected through magnetic and electric fields.

An English scientist, J. J. Thomson, combined the two experiments we have just described. He was able to study the behavior of cathode rays passing through both a magnetic field and an electric field. We can think of this experiment in stages. First the cathode rays are deflected *down* as they pass through the magnetic field (Figure 8-8). The beam is deflected *up* as it passes through the electric field (Figure 8-8). It is possible to balance these fields so that the cathode rays strike the fluorescent screen at the same position as the beam does when neither field is present. This experiment measures the ratio of the electric charge, *e*, to the mass, *m*, of the particles in the cathode rays.

Thomson used many different discharge tubes in his experiments. He changed the metal of the electrodes. He placed different gases in the tube. For all experimental arrangements, the charge to mass ratio, e/m, for cathode rays was always the same. Thomson referred to cathode rays as **electrons** and found that the ratio, e/m, for electrons is a large number. There are two interpretations. Either the charge e is a relatively large number or the mass m is a relatively small number. In Chapter 6, page 90, we discussed Millikan's experiment to measure the charge on the electron. We can combine the results of Millikan's experiment and Thomson's experiment to obtain numerical values for the charge and for the mass of the electron.

Thomson experiment $e/m = 1.76 \times 10^{8}$ coulombs/gram

Millikan experiment $e = 1.60 \times 10^{-19}$ coulomb/electron

A simple calculation gives us the mass of the electron

$$m = \frac{1.60 \times 10^{-19}\ \text{coulomb/electron}}{1.76 \times 10^{8}\ \text{coulombs/gram}}$$

$$m = 9.1 \times 10^{-28}\ \text{gram/electron}$$

We have talked in terms of molar masses for the elements. We can do the same for the electron.

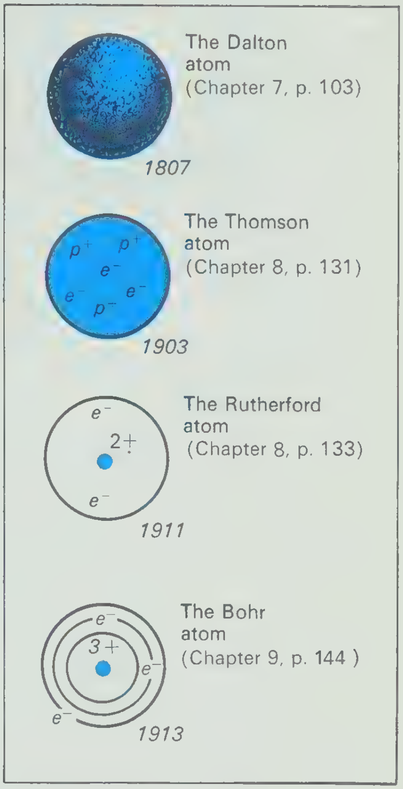
Molar mass (electron)

$$= 9.1 \times 10^{-28}\ \text{gram/electron} \times 6.0 \times 10^{23}\ \text{electrons/mole}$$

$$= 5.5 \times 10^{-4}\ \text{gram/mole}$$

The electron has much less mass than the lightest atom, the hydrogen atom.

Molar mass (hydrogen atom) = 1.008 grams/mole


The Dalton atom (Chapter 7, p. 103)
1807
The Thomson atom (Chapter 8, p. 131)
p^+
p^+
e^-
e^-
e^-
p^+
1903
The Rutherford atom (Chapter 8, p. 133)
e^-
2+
e^-
1911
The Bohr atom (Chapter 9, p. 144)
e^-
3+
e^-
e^-
1913

Atomic models (historical).

8-3 The Discovery of the Proton

Thomson was able to carry out the same sort of measurement for another set of particles that are present in a gas discharge tube. We have not yet mentioned them in our discussion. If the cathode in a gas discharge tube has holes in it, careful observation shows that some kind of particles move toward the cathode. (Remember that

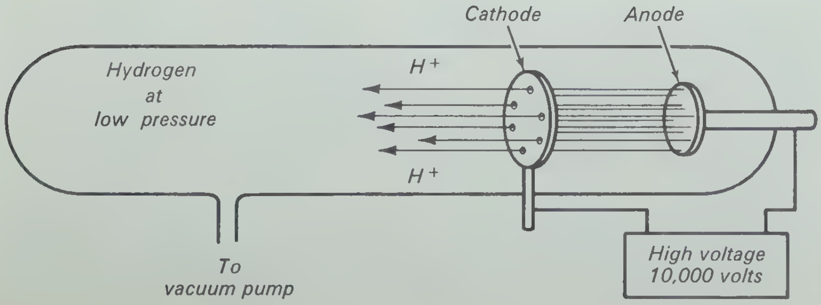

Cathode
Anode
Hydrogen at low pressure
H^+
H^+
To vacuum pump
High voltage 10,000 volts

FIGURE 8-9

Canal rays.

cathode rays or electrons travel *from* the cathode toward the anode.) Some of the particles moving toward the cathode pass through the holes as indicated in Figure 8-9. Their behavior in electric and magnetic fields indicates that they carry a positive electric charge. Thomson measured the charge to mass ratio, e/m, for these positive ions. This ratio was found to be much smaller than e/m for electrons. More important, the e/m values depended on the gas in the discharge tube. The charge to mass ratio for electrons did not depend on the nature of the gas. Comparison of the experiments that were made on these two kinds of particles is revealing.

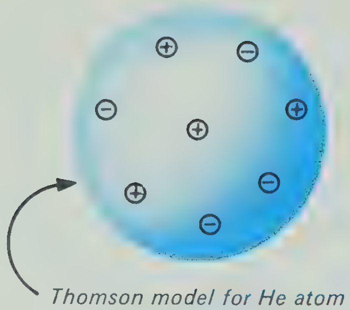


FIGURE 8-10

Thomson atom.

In a gas discharge tube, electrons and positive ions are formed. Electric current passes through the gas as these charged particles move towards the electrodes. The charge to mass ratio for these ions can be measured by studying their behavior in electric and magnetic fields. Table 8-2 summarizes the experimental results.

TABLE 8-2

Experimental Results for the Positive and Negative Ions Formed in Gas Discharge Tubes

Electric Charge of Ion	Charge to Mass Ratios, e/m	Characteristics
Negative	large numbers	Same values for all gases.
Positive	small numbers	Different values depending on gas in discharge tube.

Thomson interpreted these results in this manner. When sufficient energy is available in the gas discharge tube, the gas is ionized. We can illustrate this with some equations.

$$H_2(g) \longrightarrow 2H(g)$$
$$H(g) \longrightarrow H^+(g) + e^-$$
$$He(g) \longrightarrow He^+(g) + e^-$$

Particles with positive and negative charge form. The e/m values for the particles with negative charge are always the same because the same particle, the electron, forms in each case. The nature of the positive ion depends on the gas in the discharge tube. The e/m values differ from one gas to another. The e/m value for the hydrogen ion was the largest that Thomson found for any of the positive ions. He made the reasonable assumption that the charge on the hydrogen ion was equal to the charge on the electron but opposite in sign. The mass value can be calculated and is almost the same as the mass of the hydrogen atom. This particle is called the **proton.**

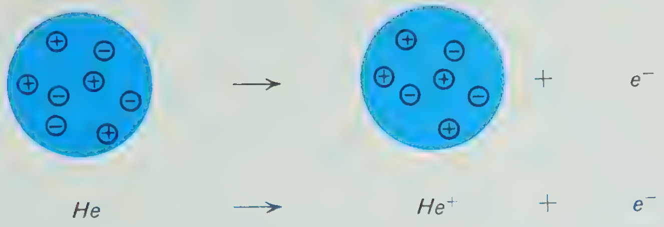


FIGURE 8-11

Ionization of helium atom (Thomson's model).

8-4 The Thomson Model for the Atom

Thomson was the first to propose a detailed model of the atom. He pictured all atoms as made of positively charged protons plus negatively charged electrons. In the neutral atom, there are equal numbers of these two kinds of particles. When energy is supplied to an atom, an electron is given up. The electron, or cathode ray, is always the same. The positive ion that is formed depends on the kind of atoms in the gas. Thomson's view of atomic structure is illustrated in Figure 8-10. A helium atom is used as the example. The molar mass for helium is very close to 4 grams. Thomson proposed that the helium atom contained 4 protons. Since each proton has one unit of mass, four protons would furnish the mass for helium. Thomson's atom also contained four electrons. Electrons have such low mass that they contribute little to the mass of a helium atom. The electrons, however, provide negative electric charge to the atom. Figure 8-11 illustrates the ionization of a helium atom. Thomson's proposal was an important step in the growth of the atomic model. It was the first real change from Dalton's simple view of atomic structure. Dalton pictured an atom as a hard sphere. Thomson's model failed because it did not provide any explanation for the line spectrum of an element. Still, his ideas provided the basis for another group of experiments.

8-5 The Discovery of X Rays and Radioactivity

While studying a variety of gas discharge tubes in 1895, a German scientist, Röntgen, provided an explanation for some observations that other scientists had overlooked. We have already mentioned the greenish fluorescence from the glass of a gas discharge tube. Röntgen discovered that air some distance from the tube was ionized when this greenish glow began. He could show easily that the ionization was not caused by the green light. A piece of paper stops the green light but does not change the ionization. Apparently a new phenomenon was being observed.

Röntgen invented the name X rays to explain his observation. When the cathode rays hit the glass of the discharge tube, X rays were formed. We know today that he discovered a form of light with very high energy. The frequency for X rays is much higher than

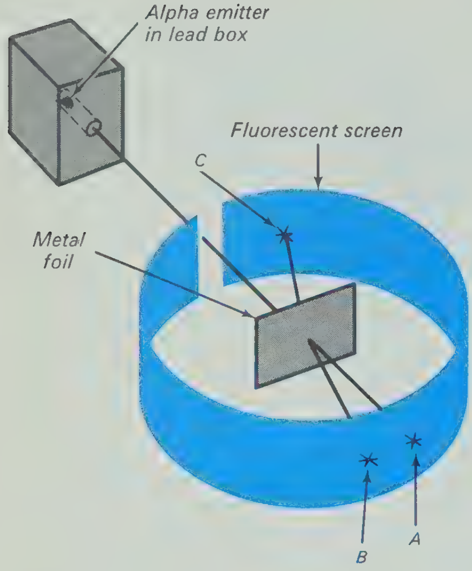


FIGURE 8-12

The Rutherford Experiment.

the frequency for visible light. The wavelengths for X rays are much smaller than the wavelengths for visible light. The fact that X rays are not readily stopped by matter has led to several very important applications. Your dentist has undoubtedly made an X-ray picture of your teeth. X rays are absorbed more by the high density material in your teeth than by the low density tissues of your cheek and gums. Your teeth cast a shadow on the film. The dentist can easily tell if you have any hidden cavities in your teeth. The same principle is involved in taking an X-ray picture of a broken bone or finding a crack in a piece of steel.

Many scientists began to study the effects of X radiation. The fact that X-ray emission occurred at the same time the green fluorescence in the glass was observed raised the question:

Is fluorescence always accompanied
by the emission of X rays?

It was known that certain substances fluoresced when exposed to sunlight. The question could be answered readily by some simple experiments. Expose a fluorescent substance to sunlight. Place it next to a photographic film, wrapped in black paper to exclude light. Develop the film to see if any radiation passed through the paper.

In the winter of 1896 a French scientist, Becquerel, was trying this kind of experiment with a uranium compound. Becquerel knew that uranium compounds exhibited strong fluorescence. By chance there was cloudy weather for several days. To Becquerel's surprise, even in the absence of sunlight, uranium compounds caused a photographic film to darken. Here was a new phenomenon that was independent of fluorescence. Uranium compounds emitted radiation that affected a photographic film.

A large number of experiments showed that several elements in addition to uranium exhibited this behavior. Since energy is needed to affect a photographic film, it was clear that these elements were able to give up energy spontaneously. Moreover, the rate at which energy is released by a particular element could not be changed. Heating the sample, freezing the material, or carrying an element through a series of chemical reactions did not slow down or speed up the energy released from these elements. These elements have the property of undergoing **radioactive decay**. We shall discuss radioactivity in Chapter 21. For now, we only need to know a few facts about it.

Alpha particles leave radium at 10,000 miles/second, yet they travel only about 3 inches through air.

The energy released in radioactive decay may be in three forms. For some elements, very high frequency waves similar to X rays are produced. The name **gamma rays,** γ rays, is used in talking about this form of energy. In other elements, high speed electrons are released. These electrons are called **beta rays,** β rays. With the exception of their very high speeds, these electrons have the same properties as the electrons Thomson studied in gas discharge tubes. Formation of **alpha particles,** α particles, is the third way that these elements give up energy. Alpha particles have a positive electric charge of two units, 2+, and have much higher mass than beta rays. Because of their high mass, alpha particles are not easily deflected.

They travel in straight lines. Alpha particles are helium atoms that have lost two electrons.

8-6 The Rutherford Model of the Atom

Many of the important experiments dealing with radioactivity were performed by Rutherford and his co-workers. In this section we will outline one of these experiments. It deals with the way alpha particles are deflected when they pass through thin metallic foils.

First, let us look at the experiment. Then perhaps we can appreciate Rutherford's interpretation. Once more we are following the activities of science: observation, a search for regularity, and wondering why.

Figure 8-12 shows the experiment that Rutherford carried out in 1911. A sample of radioactive material was placed in the lead box on the left of the diagram. A narrow beam of alpha particles escaped through the small hole in the side of the box. Thin metal foils of different elements were placed in the path of the beam of alpha particles. A fluorescent screen was set up around the foil. When an alpha particle hit the fluorescent screen, a flash of light could be seen. Most of the high energy alpha particles passed straight through the metal foil to hit the fluorescent screen at point *A*. Occasionally an alpha particle would be deflected through a small angle to strike the screen at point *B*. Much to Rutherford's amazement, a few alpha particles were deflected through very large angles. Some would strike the screen at point *C*. In a lecture that he gave in 1936, Rutherford described his astonishment by saying: "It was about as credible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you." In every experiment, almost all the alpha particles passed straight through the foil. But there were always a few that were deflected through large angles.

Rutherford could not explain these results using Thomson's model of the atom. He knew that the positively charged alpha particle would be repelled by the positive charges that Thomson spread through his atoms. Small angle deflections, as in Figure 8-13, would not be a surprise. Large angle deflections could not be explained. Rutherford suggested that the positive charge in an atom was contained in a very small nucleus. Most of the mass would also be in the nucleus. The electrons in the atom, with their negative charges, surrounded the nucleus like a swarm of bees. The mass of an electron is so small that one could almost ignore it.

Consider once more Rutherford's alpha scattering experiment. Figure 8-14 offers a schematic explanation of what happened. Since the nucleus of the atom is so small, most of the alpha particles would not come very close to a nucleus. Alpha particles would pass through the foil without much deflection. Some of the alpha particles would pass near the positively charged nucleus. Positive electric charges repel one another. These alpha particles would be deflected through small angles. Every once in a while an alpha particle would collide almost head-on with a nucleus. These par-

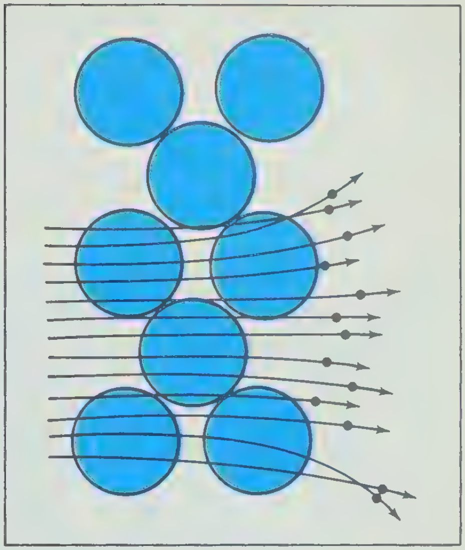


FIGURE 8-13

The scattering of alpha particles by a metallic crystal made up of Thomson atoms. Rutherford's results are *not* explained.

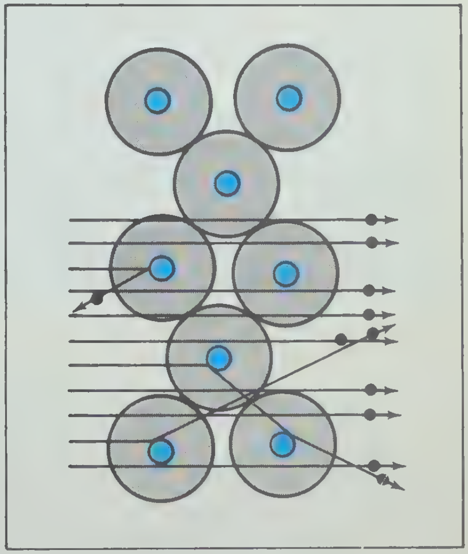


FIGURE 8-14

The scattering of alpha particles by a metallic crystal made up of Rutherford atoms. Rutherford's results *are* explained.

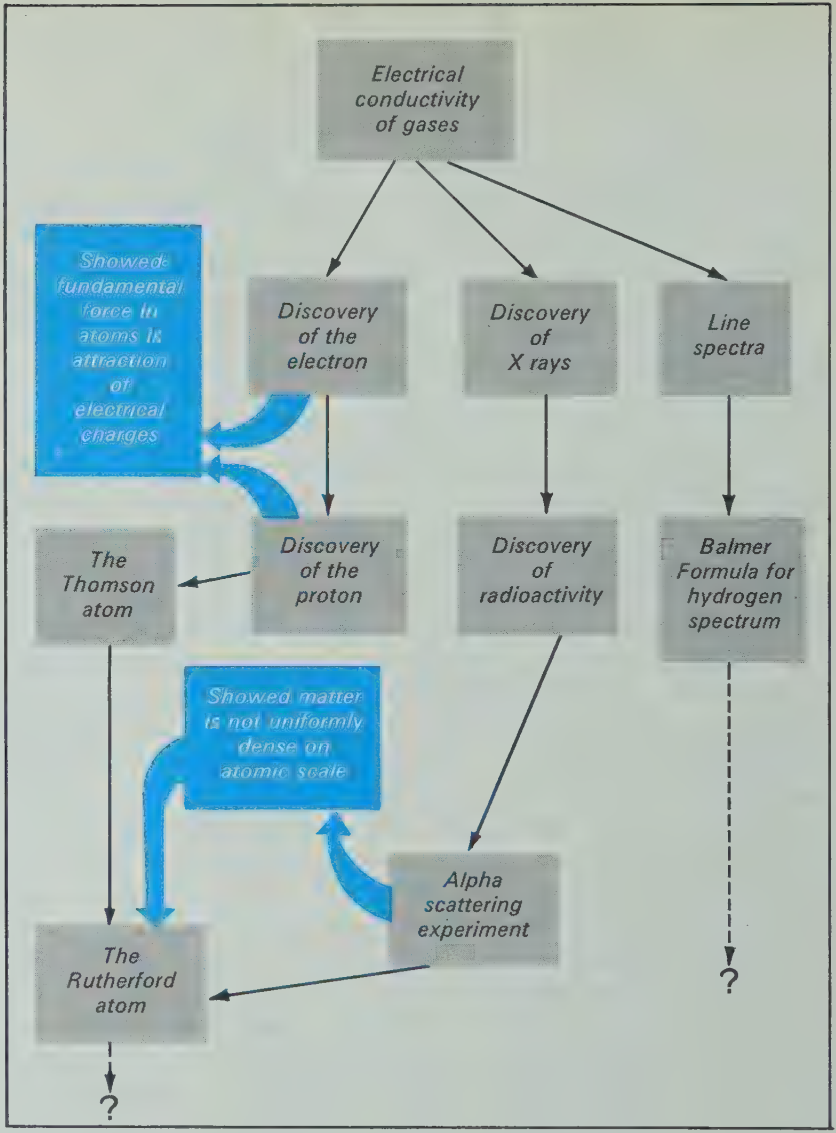

Electrical conductivity of gases
Discovery of the electron
Discovery of X rays
Line spectra
Showed fundamental force in atoms is attraction of electrical charges
The Thomson atom
Discovery of the proton
Discovery of radioactivity
Balmer Formula for hydrogen spectrum
Showed matter is not uniformly dense on atomic scale
Alpha scattering experiment
The Rutherford atom
?
?

FIGURE 8-15

The search for experimental regularity that leads to an explanation of atomic structure.

ticles would change their directions through large angles. Rutherford was able to calculate from his model the fraction of alpha particles deflected through a particular angle. The agreement between the experiments and his model was excellent. The Rutherford model proposes that the mass of an atom and its positive charge are concentrated in a nucleus that is about one hundred-thousandth of the diameter of the atom. The negative charge carried by electrons is spread throughout a much larger volume. Electrons define the size of an atom.

Another important result of the scattering experiment was the determination of the positive electric charge on the nucleus. It is easy to understand how one can measure this positive charge, but the experiment requires great care and patience. As it passes through the metal foil, an alpha particle with its 2+ charge would be deflected

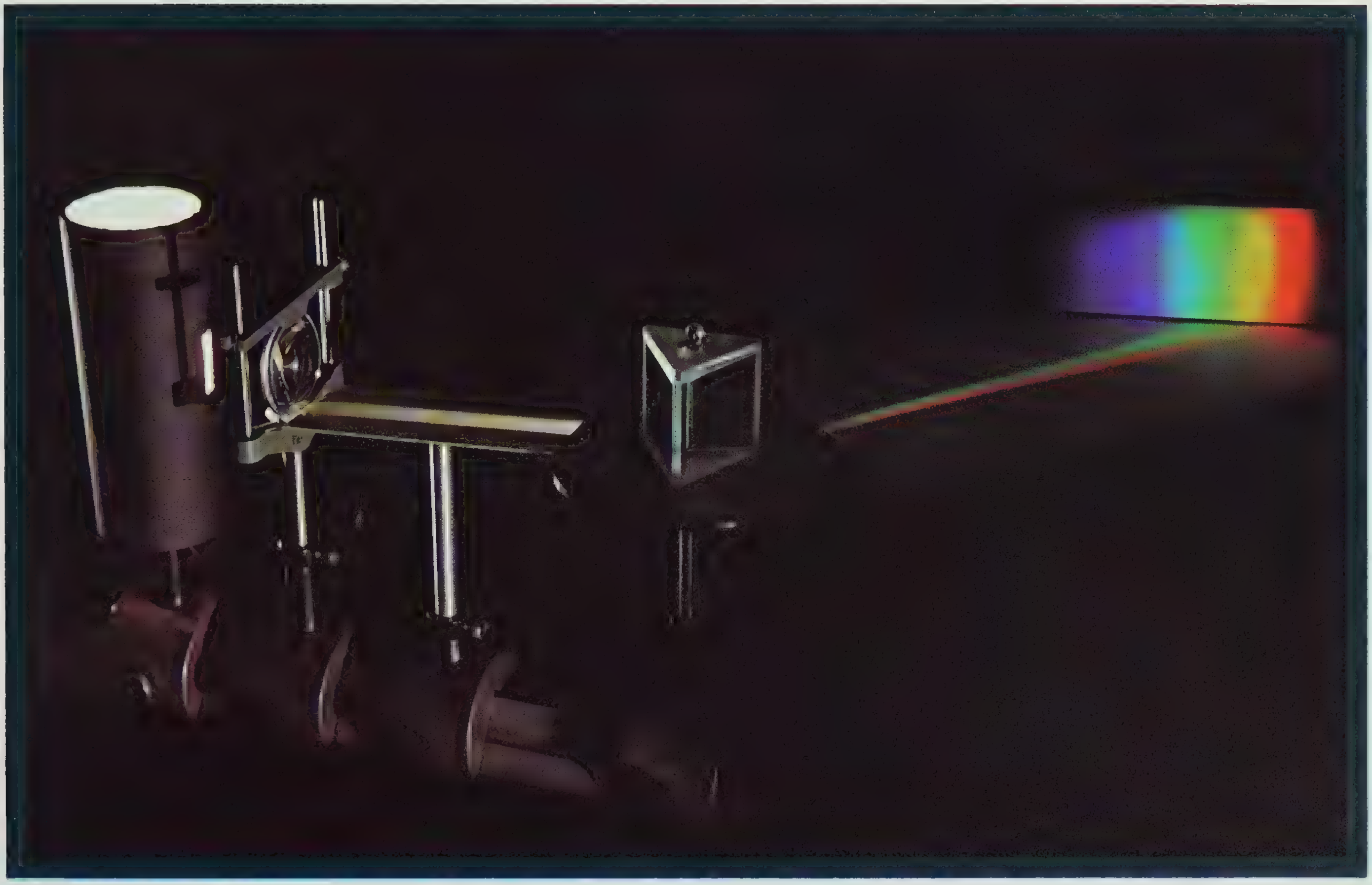


PLATE I A simple spectrograph and the spectrum of a hot tungsten ribbon.

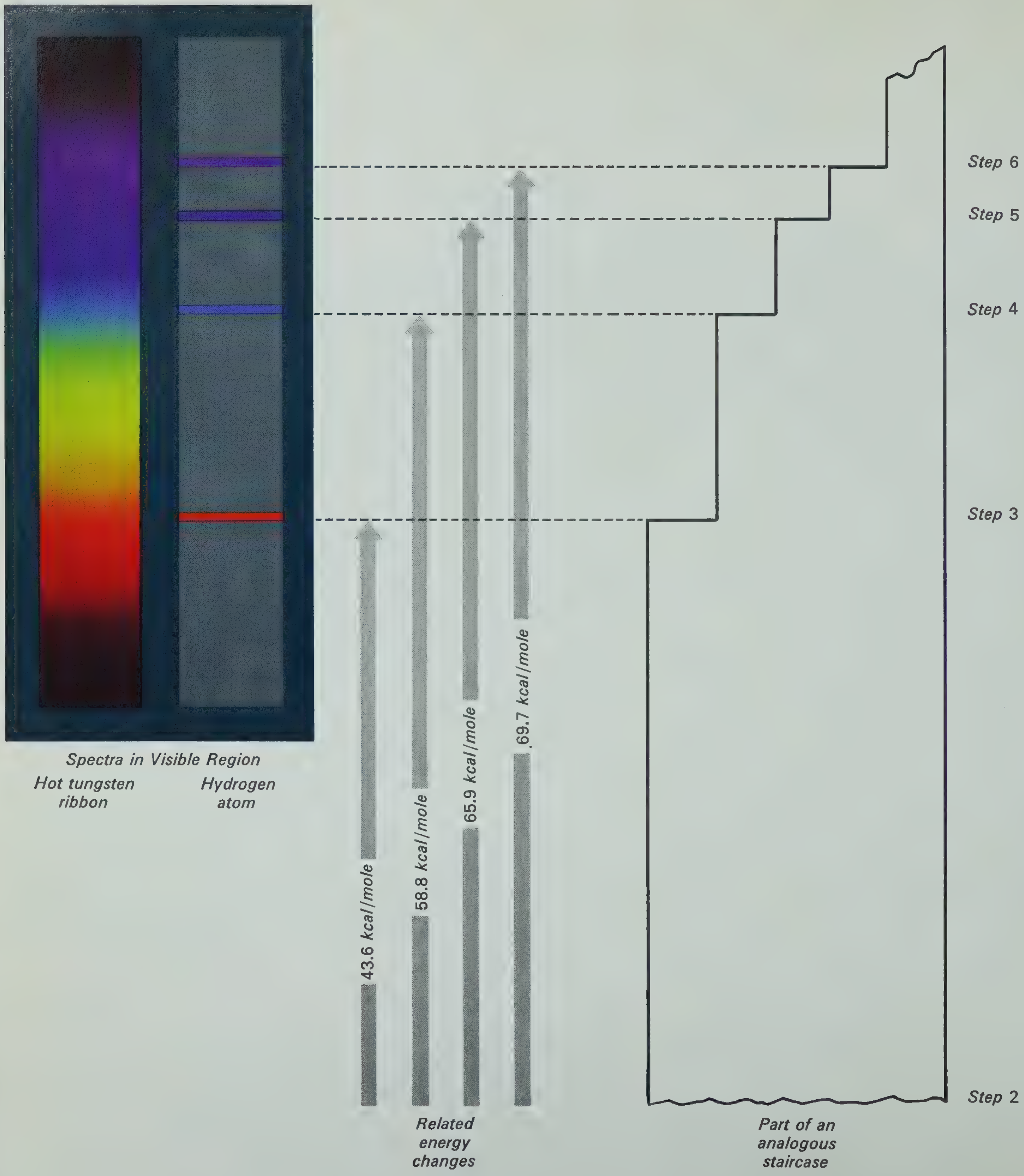

Spectra in Visible Region
Hot tungsten ribbon
Hydrogen atom
43.6 kcal/mole
58.8 kcal/mole
65.9 kcal/mole
69.7 kcal/mole
Related energy changes
Step 6
Step 5
Step 4
Step 3
Step 2
Part of an analogous staircase

PLATE II The hydrogen atom spectrum: a clue to energy levels.

through a large angle by a nucleus with a large positive charge. For small nuclear charge, the alpha particle would not be deflected as much. These experiments show that the positive charge on the nucleus of an atom is always an integer. More important, the nuclear charge corresponds exactly to the position of an element in the Periodic Table. In talking about the Periodic Table in the last chapter we referred to the numerical order of the elements. The significance is now clear. The numerical order is called the **atomic number** of the element. *The atomic number of an element is equal to the positive charge on its nucleus.* For hydrogen this number is 1. The nucleus of a hydrogen atom carries a 1+ charge. For calcium the atomic number is 20. The calcium nucleus has a charge of 20+. The form of the Periodic Table is tied directly to the structure of atoms. In the next chapter we will find out more about this subject.

8-7 The Neutron and Isotopes

The Rutherford model of the atom places protons in the nucleus with electrons surrounding it. Chemical properties of an element depend almost entirely on the behavior of these electrons. Before discussing that subject let's briefly describe the nucleus of an atom as it is understood today. We jump from 1911 to 1932 in order to do this.

In that year a different type of scattering experiment was being studied. These experiments could only be explained by postulating a new type of particle with zero electric charge. Its mass is very close to the proton mass. It is called the **neutron.** Like the proton, the neutron is found in the nucleus. With the neutron we can build up atoms for all the elements. Table 8-3 describes the building blocks for all atoms.

TABLE 8-3

Charge and Mass of Electron, Proton, and Neutron

Particle	Charge	Approximate mass relative to proton
Electron	1−	$^1/_{1840}$
Proton	1+	1
Neutron	0	1

Each atom has a nucleus made up of protons and neutrons. All atoms of a particular element have the same electric charge on the nucleus. This means *all atoms of a particular element have the same number of protons in the nucleus.*

The protons plus the neutrons account for the mass of the nucleus. The **mass number** of the nucleus equals the number of protons plus the number of the neutrons. The mass number is an integer which has approximately the same value as the molar mass. Not all atoms of an element have the same mass number.

Atoms that have the same nuclear charge but different nuclear masses are called **isotopes.** *Isotopes have the same number of protons but different numbers of neutrons in the nucleus.* An example will help make this statement clear.

Lithium is the element with atomic number equal to three. All lithium atoms have three protons in their nuclei. Some lithium atoms have mass number of six. Other lithium atoms have mass number of seven. The isotope, Li-6, has three protons and three neutrons in the nucleus. The isotope, Li-7, has three protons and four neutrons in the nucleus. Each lithium isotope has three electrons in the neutral atom. Table 8-4 summarizes the structure of some common isotopes. The neutrons in a nucleus apparently provide attractive forces to hold the nucleus together. These forces are not yet understood. However, the attractive forces must predominate over the electrical repulsions between the protons in the nucleus.

TABLE 8-4 Structure of Some Common Isotopes

				Nucleus			Mass of Atom	Number of Electrons in Neutral Atom
Isotope	Abundance in Nature	Atomic Number	Mass Number	Number of Protons	Number of Neutrons	Electric Charge	$C^{12} = 12.0000$	
Hydrogen-1	99.984%	1	1	1	0	1+	1.0078	1
Hydrogen-2	0.016	1	2	1	1	1+	2.0141	1
Helium-3	1.3×10^{-4}	2	3	2	1	2+	3.0160	2
Helium-4	100	2	4	2	2	2+	4.0026	2
Lithium-6	7.42	3	6	3	3	3+	6.0151	3
Lithium-7	92.58	3	7	3	4	3+	7.0160	3
Beryllium-9	100	4	9	4	5	4+	9.0122	4
Boron-10	19.61	5	10	5	5	5+	10.0129	5
Boron-11	80.39	5	11	5	6	5+	11.0093	5
Carbon-12	98.893	6	12	6	6	6+	12.0000	6
Carbon-13	1.108	6	13	6	7	6+	13.0034	6
Nitrogen-14	99.63	7	14	7	7	7+	14.0031	7
Nitrogen-15	0.37	7	15	7	8	7+	15.0001	7
Oxygen-16	99.76	8	16	8	8	8+	15.9949	8
Oxygen-17	0.04	8	17	8	9	8+	16.9991	8
Oxygen-18	0.20	8	18	8	10	8+	17.9992	8
Fluorine-19	100	9	19	9	10	9+	18.9984	9
Chlorine-35	75.53	17	35	17	18	17+	34.9689	17
Chlorine-37	24.47	17	37	17	20	17+	36.9659	17
Uranium-235	0.72	92	235	92	143	92+	235.0439	92
Uranium-238	99.27	92	238	92	146	92+	238.0508	92

Most chemical elements consist of a mixture of isotopes. For example, oxygen has three stable isotopes. The nuclear charge is 8+ for each isotope. The mass numbers are 16, 17, and 18. The kind of atom having mass number 16 is the most abundant. The chemical properties for these three isotopes depend almost entirely on the nuclear charge and not on the nuclear mass. Chemists can speak about the reactions of oxygen without specifying the isotope. The molar mass you see in a Periodic Table is a weighted average derived from the masses of the isotopes, allowing for their relative abundance.

8-8 Review

The search for an explanation for atomic structure is surely one of the best examples of how science grows. From an initial curiosity about the conductivity of electricity in gases at low pressure to the discovery of the neutron, one experiment led to another. Sometimes questions, answers, and more experiments followed rapidly on each other; sometimes answers did not appear for many years. In this chapter we have outlined briefly the most significant of the experiments. We can summarize this search with the block diagram in Figure 8-15. Some of the experiments seemed to be unrelated to the mainstream, only to provide an important link at a later date. In the next chapter we will see how the question marks in this diagram were removed. The important building blocks for atoms are electrons, protons, and neutrons. The electrons in an atom occupy a volume about 10^{12} times larger than the nucleus of the atom. A neutral atom has Z protons in the nucleus and Z electrons in the volume around the nucleus. The symbol Z is used to represent the *atomic number* of an element. Except for the simplest atom, hydrogen, the nuclei of all atoms contain neutrons. The number of neutrons in a nucleus is designated by the symbol N. The *mass number* for an atom is equal to $Z + N$, which is approximately equal to the mass of the atom.

All atoms of an element have Z protons in the nucleus.

Atoms of the same element may have different mass numbers, that is, different numbers of neutrons in the nucleus.

Atoms with the same Z but different N are called *isotopes.*

Questions and Problems for Chapter 8

1

Use the data about water waves on page 124 to calculate how fast the wave is moving, in miles per hour.

2

The electromagnetic waves used in FM broadcasting by radio or television have frequencies of approximately 100 megacycles per second. In standard AM radio broadcasting, the frequency is approximately 1 megacycle per second.

Use the relationship $\lambda = c/\nu$, where c = velocity of light = 3.0×10^{10} cm/sec, to calculate the wavelengths used in AM and FM broadcasting. Compare these values with the wavelengths for red and blue light in Table 8-1.

3

The pressure in a gaseous discharge tube is approximately 10^{-2} atmosphere when glow discharge begins. As the pressure is decreased, the cathode dark space increases in length. At about 10^{-6} atmosphere pressure, the glow discharge disappears.

How many molecules would there be in one cubic centimeter of gas when the glow first appears?

How many molecules would there be in one cubic centimeter of gas when the glow disappears?

4

How many electrons are needed to furnish a mass of one gram? What would be the mass of a mole of electrons?

5

How much electric charge is provided by one mole of electrons? By one mole of protons?

6

From the molar mass of the electron and the molar mass of the hydrogen atom, calculate the molar mass of the proton. Calculate the ratio of proton mass to electron mass.

7

The nucleus of an aluminum atom has a diameter of about 2×10^{-13} cm. The atom has an average diameter of about 3×10^{-8} cm. Calculate the ratio of the diameters.

8

The radius of a carbon atom in many compounds is 0.77×10^{-8} cm. If the radius of a Styrofoam ball used to represent the carbon atom in a molecular model is 1.5 cm, how much of an enlargement is this?

9

Platinum and zinc have the same number of atoms per cubic centimeter. Would thin sheets of these elements differ in the way they scatter alpha particles? Explain.

10

Assume that the nucleus of the fluorine atom is a sphere with a radius of 5×10^{-13} cm. Calculate the density of matter in the fluorine nucleus.

11

An average dimension for the radius of a nucleus is 1×10^{-13} cm and for the radius of an atom is 1×10^{-8} cm. Determine the ratio of atomic volume to nuclear volume.

12

Which would have a larger charge to mass ratio, a Na^+ or a K^+ ion?

13

Suppose, in the Thomson model for the atom, that the charge of the proton is uniformly spread throughout the volume for one hydrogen atom. Using the value 10^{-8} cm for the radius of the hydrogen atom and 1.6×10^{-19} coulomb for the unit electric charge, calculate the charge density in coulombs/cm^3.

14

Repeat Problem 13 for the Rutherford model for the hydrogen atom. The proton is now the nucleus of the atom, with a radius of approximately 10^{-13} cm.

15

Use your answers from Problems 13 and 14 to discuss qualitatively the scattering of alpha particles by Thomson atoms and by Rutherford atoms.

16

Which of the following statements is FALSE? The atoms of oxygen differ from the atoms of every other element in the following ways:

(a) the nuclei of oxygen atoms have a different number of protons than the nuclei of any other element;
(b) atoms of oxygen have a higher ratio of neutrons to protons than the atoms of any other element;

(c) neutral atoms of oxygen have a different number of electrons than neutral atoms of any other element;

(d) atoms of oxygen have different chemical behavior than do atoms of any other element.

17

List the number and kind of fundamental particles found in a neutral lithium atom that has a nucleus with a nuclear charge three times that of a hydrogen nucleus and with approximately seven times the mass.

18

Helium, as found in nature, consists of two isotopes. Most of the atoms have a mass number 4, but a few have a mass number 3. For each isotope, indicate the:

(a) atomic number;
(b) number of protons;
(c) number of neutrons;
(d) mass number;
(e) nuclear charge.

19

On a separate sheet of paper copy and complete the following table. Do not write in this book.

Element	Atomic No.	Particles Per Atom			Mass Number
		Protons	Electrons	Neutrons	
Aluminum (Al)	13				27
Beryllium (Be)		4			9
Bismuth (Bi)	83				209
Calcium (Ca)			20	20	
Carbon (C)		6		6	
Fluorine (F)			9		19
Phosphorus (P)	15			16	
Iodine (I)			53		127

20

How do isotopes of one element differ from each other? How are they the same?

21

Use the exact masses and the percent abundance in Table 8-4 for Cl-35 and Cl-37 to calculate the average molar mass for atomic chlorine.

Models for Atomic Structure

9

The experiments discussed in Chapter 8 presented exciting new ideas to scientists early in this century. Step by step these discoveries led from one model for the atom to another as scientists searched for explanations of their experiments. The best model that we know for the atom has its origin in a proposal by Niels Bohr in 1913. Bohr's model was modified in the 1920's into the quantum theory of atomic structure. In this chapter we will explore these models.

First let us see why Rutherford's model of the atom had to be changed. There were two sets of experimental facts that contradicted each other. The nuclear atom proposed by Rutherford provided an explanation for the experiments on the scattering of alpha particles. This model, however, was not in agreement with a large number of experiments dealing with electric charge. These experiments had shown many times that objects with unlike electric charges attract each other. If there is no force holding them back, the objects move towards each other. When these objects touch, their electric charges are neutralized. Rutherford's model had electrons with negative charge around a very small positively charged nucleus. According to all experiments dealing with electric charge, electrons should be pulled into the nucleus in a very short period of time.

A strange puzzle indeed! The best model for the atom suggested an unstable structure. And yet, atoms do not collapse. Evidently something was wrong with the model or with the experimental facts. The experiments were repeated. The facts remained the same.

> Objects with opposite electric charge attract each other.
>
> Only a small fraction of alpha particles are deflected by a thin metal foil.

The time was ripe for someone of great vision and imagination to provide an explanation for the many experiments dealing with atoms. The Danish physicist Niels Bohr was such a person. He proposed a new model that did not contradict the known facts. But in doing this, he had to make the revolutionary suggestion: particles as small as electrons and protons and atoms do not behave in the same manner as the large objects we deal with in the laboratory. He suggested that atoms are stable even though the positive and negative electric charges in atoms seemed to have nothing to hold them apart. With this assumption, Bohr was able to keep the nuclear atom proposed by Rutherford to explain the experiments on alpha scattering. In addition, Bohr's model was in agreement with the line spectrum of hydrogen. For the first time a model for the atom could provide an explanation for the spectrum of an element.

The discussion of spectra that we started in Chapter 8 will help us understand the reasoning that led Bohr to his atomic model.

9-1 Ionization Energy and the Hydrogen Spectrum

Several important features of the hydrogen spectrum were pointed out in Section 8-1, page 122. First, hydrogen atoms emit light of certain frequencies. Second, the lines on the photographic film are spaced systematically. A definite frequency of light can be associated with each of these lines. Let us look at these spectral lines to see if they can be related to the energy of the atom. The hydrogen atom, just before emission of light, has a certain energy, E_2. Light of frequency, ν, is emitted, carrying away energy, $h\nu$. The hydrogen atom now must have a smaller amount of energy, E_1. The energy lost by the hydrogen atom must be equal to the energy of light carried away.

$$\Delta E = E_2 - E_1 = h\nu$$

All observed values for $h\nu$ are smaller than the ionization energy for the hydrogen atom, 313.6 kcal/mole. This fact suggests that less energy is involved in producing the lines of the spectrum than is needed to remove an electron completely from the hydrogen atom.

A diagram will help us describe some energy changes that the hydrogen atom undergoes. The energy of the hydrogen atom is represented as the lower line in Figure 9–1. The process of ionization is shown by the vertical arrow.

$$\text{H(g)} + 313.6\ \text{kcal} \longrightarrow \text{H}^+\text{(g)} + e^-$$

The particles produced, H^+(g) and e^-, have considerably more energy than the original hydrogen atom. The horizontal line representing the energy for these particles is the higher line in the figure. Energy is absorbed during ionization of an atom. The hydrogen ion and the electron can recombine to form a neutral hydrogen atom. When this occurs, energy is emitted as shown in Figure 9-2.

$$\text{H}^+\text{(g)} + e^- \longrightarrow \text{H(g)} + 313.6\ \text{kcal}$$

We have already pointed out that there are many lines in the hydrogen spectrum. More important we saw that the energy of these spectral lines never exceeded the ionization energy, 313.6 kcal/mole. There is an important idea here. Perhaps the line spectrum for

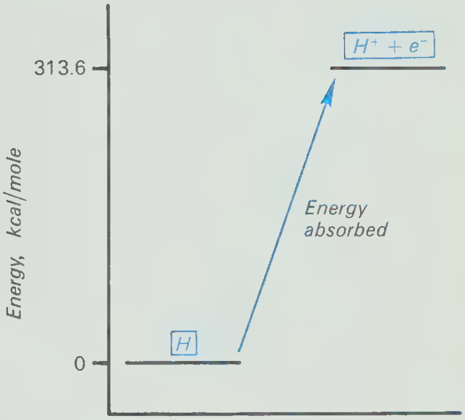


FIGURE 9-1

Ionization of the hydrogen atom.

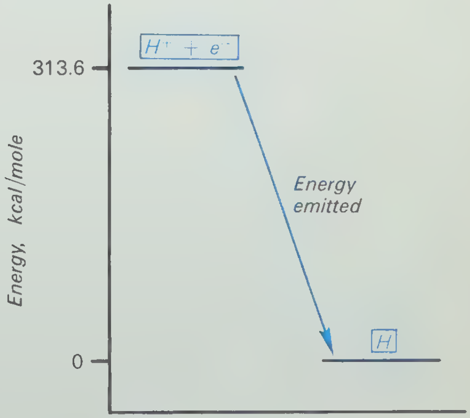


FIGURE 9-2

Recombination of H^+ and e^- to form the hydogen atom.

hydrogen means that there are intermediate energy states for the hydrogen atom, between the two states we call the hydrogen atom, H, and the ionized state, H^+ and e^-. How can we deduce from the spectrum what energy states a hydrogen atom can have?

9-2 A Model That Explains the Hydrogen Spectrum

If there are certain energy states for a hydrogen atom, perhaps we can use a staircase as a model. Each step on the staircase will represent a different energy state. Imagine many children going up and down this staircase. If a child goes higher on the staircase, his potential energy increases. The work that is necessary to move up a staircase is transformed into energy of position. Occasionally one of the children jumps down the staircase. His potential energy is converted into energy of motion. When he lands on a stair, the energy is converted to different forms, primarily heat and sound. Suppose that we cannot see the staircase. We can hear the children calling out or signaling the change they make going up or down the staircase. We never learn which stair they are on. They only announce the change they are making. We hear numbers like "one, one, one, three, four, two, one, two, three, four, one . . . ." Suppose that these are the only numbers heard. They form the energy spectrum for this staircase. We can easily construct the staircase the children are playing on even though we cannot see it. It would look like the diagram in Figure 9-3. We can be fairly sure that the staircase is only five levels high because the children never announce a jump or change larger than four steps. We assume that the children could jump more than four steps if the staircase were longer.

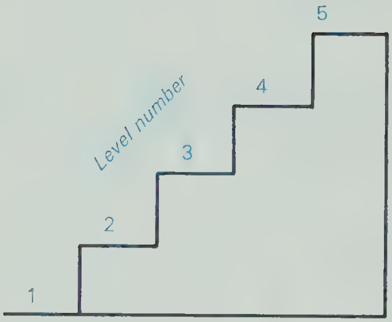


FIGURE 9-3

The hidden staircase.

There are two points we want to emphasize in this model. First, the children always change an integral number of steps. There is no way for them to move up or down by a half or a third of a level. Second, a change from level 5 to level 3 would be called out in the same way as a change from level 2 to level 4. The signal we receive is "2" for each of these changes.

EXERCISE 9-1

List all possible changes on this staircase. List them systematically. For example, for the changes that begin on level 1, write 1 ⟶ 2, 1 ⟶ 3, 1 ⟶ 4, and 1 ⟶ 5. For changes that end on level 1, write 5 ⟶ 1, 4 ⟶ 1, 3 ⟶ 1, and 2 ⟶ 1. Next to these indicate the size of each change. Repeat for levels 2, 3, and 4.

9-3 The Hydrogen Atom

The example in Section 9-2 outlined the way to draw a hidden staircase from its observed spectrum. It might be useful to follow the same procedure for the hydrogen atom. The observed spectral lines for hydrogen might tell us the energy changes made by the electron in the hydrogen atom. The hydrogen spectrum in the ultraviolet region is given in Table 9-1. The energy listed for each spectral line is the size of the energy change that the electron in the hydrogen atom signals to us. We can draw a diagram of the hydrogen staircase from the energies listed in Table 9-1.

TABLE 9-1

The Ultraviolet Spectrum for Atomic Hydrogen

$\Delta E = h\nu$

Wavelength, λ (Ångstroms)	Frequency, ν (cycles/second)	Energy, $h\nu$ (kcal/mole)
1216	2.47×10^{15}	235.2
1026	2.92×10^{15}	278.8
973	3.08×10^{15}	294.0
952	3.15×10^{15}	301.1
938	3.20×10^{15}	304.9
934	3.22×10^{15}	307.2
930	3.24×10^{15}	308.7

1 Ångstrom = 1×10^{-8} cm

We will assign the number 1 to the lowest level. The next level, number 2, is drawn 235.2 kcal/mole higher and so on. The top level of the staircase is assigned the number ∞. This level corresponds to the ionized state of a hydrogen atom, H^+ and e^-. We can build our

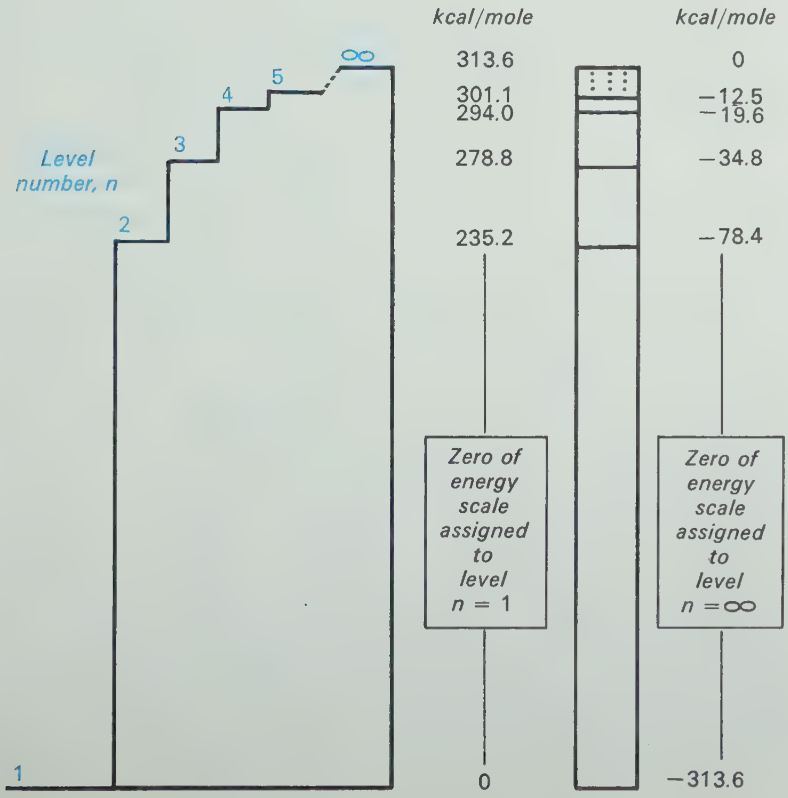

kcal/mole
kcal/mole
∞
5
4
3
2
1
Level number, n
313.6
301.1
294.0
278.8
235.2
0
0
−12.5
−19.6
−34.8
−78.4
−313.6
Zero of energy scale assigned to level n = 1
Zero of energy scale assigned to level n = ∞

FIGURE 9-4

The hidden staircase in the hydrogen atom.

staircase by indicating a level for each of the energy values in Table 9-1. The result, shown in Figure 9-4, is a staircase all right. But it is a peculiar one! The steps are not the same height. They get smaller and smaller the higher we go. Between level 5 and level ∞, there are many energy levels so close together that it is difficult to draw them. The electron in one of the higher energy states can change to a lower energy level. Energy in the form of light will be released. As with the children jumping down the staircase, the electron must change from one energy level to another. There are no halfway resting points in either case. Complete Exercise 9-2 before reading further.

EXERCISE 9-2

Suppose that electrons change from the higher energy states to the one designated No. 2. Use the energy values in Table 9-1 to make a list of the energy changes that occur. Compare your list with the Balmer spectral lines in Exercise 8-1, page 127.

9-4 Bohr's Model for the Hydrogen Atom

We are ready to look at the model for the hydrogen atom that explains the hydrogen spectrum. Bohr adopted Rutherford's nuclear atom and proposed that the electron arrangement in an atom is fixed by the energy of the atom. He also proposed that only certain energy levels are possible. These levels are called **stationary states.** As long as the electron is in one of the stationary states, no energy is given off. When an electron changes from a higher to a lower stationary state, energy in the form of light is emitted. The spectral line we see is caused by the emitted light. Finally, Bohr *assumed* that the electron could stay in the lowest energy state indefinitely. Bohr saved the atom from catastrophe! Negatively charged electrons would not fall into the positively charged nucleus. We accept this surprising assumption because Bohr's model has proved so successful.

These ideas were quite revolutionary. They were accepted only because Bohr was able to calculate the hydrogen atom energy levels exactly. Knowing the energy levels, Bohr could calculate the spectrum for the hydrogen atom. The spectral lines in the ultraviolet part of the hydrogen spectrum correspond to the electron changing from the higher energy states to level 1 in Figure 9-4. You have just calculated another set of spectral lines in Exercise 9-2. They are found in the visible portion of the hydrogen spectrum. These spectral lines are the Balmer lines and appear when an electron changes from high energy states to level 2. Another set of lines in the hydrogen spectrum is in the infrared region. As you may have guessed, they arise when electrons in high energy states change to level 3.

From 1913 to 1927 there was great turmoil in scientific circles as Bohr's ideas were discussed. During this time several physicists developed the idea that an electron has wavelike properties. When this idea was combined with Bohr's assumption on the behavior of very small particles, the quantum theory of atomic structure was born. We still use this theory of the behavior of matter. The principal equation in this theory requires more mathematics than you have studied. For our purposes it is enough to know the results of these calculations.

Schrödinger's quantum-mechanical equation

$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

The first result is the same whether calculated by Bohr's procedure or by the wave theory. The energy levels or stationary states for the hydrogen atom are given by this formula.

$$E_n = \frac{-313.6\ \text{kcal/mole}}{n^2}$$

E_n is the amount level n is below level ∞ in Figure 9-4. The integer n takes on the values 1, 2, 3 . . . . It is called the **principal quantum number.** On page 141, we stated that the energy of the light emitted is given by the equation

$$E_2 - E_1 = h\nu = \Delta E$$

We can write a general expression for the frequency of the spectral lines for hydrogen by combining the last two equations.

$$\Delta E = h\nu = 313.6\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\ \text{kcal/mole}$$

When $n_1 = 1$ and $n_2 = 2, 3, 4 \ldots$, the energies correspond to the ultraviolet spectrum. When $n_1 = 2$ and $n_2 = 3, 4, 5 \ldots$, we obtain the spectral lines in the visible portion of the spectrum.

The second result that we get from the wave theory equations does not appear in Bohr's calculations. For each value of the principal quantum number, n, there are n^2 ways to solve the wave equation. For example, if $n = 1$, the equation can be solved in 1^2 or 1 way. If $n = 2$, the equation can be solved in 2^2 or 4 ways. Each solution is called a **wave function.** The square of this function has an important meaning for us. It describes how the **probability** of finding an electron changes from place to place. We cannot trace an exact path as the electron moves and therefore the notion of an orbit or path for an electron is discarded. Instead we add up the probability of finding the electron at various points around the nucleus. The word **orbital** has been chosen to describe the sum of these probabilities. An orbital can be thought of as a region of space around the nucleus of the atom. An orbital represents the space in which an electron is most likely to be found. In the next section we will discuss orbitals in some detail. Before doing that, however, there is one other important point to consider.

In Chapter 7, the discussion of the noble gas family brought out the fact that these elements show almost no chemical reactivity. We also saw that the ionization energies for these elements are very high. The atomic structure for the noble gases must be particularly stable. Table 9-2 compares the number of orbitals in the hydrogen atom with the number of electrons in each noble gas.

TABLE 9-2

Stable Electron Populations of Noble Gases and the Hydrogen Atom Orbitals

The Noble Gases		
element	number of electrons	differences
Helium	2	2
Neon	10	10 − 2 = 8
Argon	18	18 − 10 = 8
Krypton	36	36 − 18 = 18
Xenon	54	54 − 36 = 18
Radon	86	86 − 54 = 32

The Hydrogen Atom		
n	number of orbitals, n^2	$2 \times n^2$
1	1	2
2	4	8
3	9	18
4	16	32

Notice the last column in each section of this table. The same numbers, 2, 8, 18, and 32, appear in each column. In the left-hand section, the numbers come from experimental measurement of atomic number. In the right-hand section, the numbers are obtained by doubling the number of orbitals. We can interpret the doubling to mean that each orbital can contain a maximum of two electrons. We shall see how this assumption provides an explanation for the Periodic Table. Here is a summary of our atomic model and the experimental evidence for each statement.

Statement	Basis for Statement
1. Atoms contain a very small nucleus which has a positive electric charge. Electrons surround this nucleus.	1. Thomson's experiments, with gas discharge tubes. Rutherford's experiments, with alpha particle scattering.
2. The number of protons in the nucleus equals the number of electrons around the nucleus. This number is an integer. It is called the **atomic number.**	2. Atoms have zero electric charge. Chadwick's extension of Rutherford's scattering experiments.
3. The number of protons plus the number of neutrons in the nucleus equal the **mass number** for the atom.	3. Chadwick's discovery of the neutron.
4. The electrons in an atom can occur only in certain energy levels. The energy levels are described by a number *n*, called the principal quantum number. This number is always an integer. Small values for *n* indicate low energy values.	4. Interpretation of line spectra. Solution of the equation derived from wave theory of electron.
5. There are n^2 **orbitals** for each energy level. An orbital is a region of space around the nucleus where the electron is most likely to be found.	5. Solution of mathematical equation, called the wave equation.
6. Each orbital can have a maximum of two electrons in it.	6. An assumption which leads to the numbers 2, 8, 18, and 32, in agreement with experimental atomic numbers.

9-5 The Meaning of Orbitals

The orbital description for the electrons in an atom or molecule can be compared with the pattern of holes in a dartboard. After a dartboard has been used for a long time there are many holes near the bull's-eye. As one looks away from the bull's-eye in any direction, there is a regular decrease in the number of holes per square centimeter of the dartboard. The number of holes per square centimeter, at any distance from the bull's-eye, is a measure of the probability that the next dart will land there. The holes in the dartboard do not tell us anything about the order in which the holes were made or where the next dart will land. The situation in the atom is similar. The orbital describes the probability that an electron will be a particular distance and direction from the nucleus. The orbital does not describe how the electron moves from point to point.

One of the errors in Bohr's model for the atom was the assignment of an exact orbit for the electron. Such an orbit has meaning only if there is some way to measure the orbit. Think for a moment on how we locate an airplane or how we measure the depth of the ocean. Radar waves reflected from an airplane let us follow the airplane's path. The length of time required for sound waves to be reflected from the ocean floor tells us how deep the ocean is. On the atomic scale any device we might use to measure the electron path brings so much energy into the system that the electron path is changed! We must be happy with a fuzzy picture of where the electron might be in an atom instead of the sharply defined orbits proposed by Bohr.

Orbitals are more easily understood as drawings than as mathematical equations. These drawings show an orbital as the region around the nucleus in which the electron is most likely to be. Let us discuss orbitals in more detail now.

9-6 The Orbitals for the Hydrogen Atom

For the lowest energy level, the principal quantum number n equals 1. There is only one orbital for this energy level since $n^2 = 1$. This orbital is called the 1*s* (one *s*) orbital. It is drawn in Figures 9-5 and 9-6. The words "spherical symmetry" are used to describe the 1*s* orbital. These words mean that the probability of finding the electron at a particular distance from the nucleus is the same no matter which direction you choose in going from the nucleus. The letter *s* may help you associate "sphere" with the shape of the 1*s* orbital. In all our drawings of orbitals, the shaded regions indicate the volume where we would find the electron 90–95% of the time. Remember there is always a small chance that the electron will be found farther from the nucleus than our drawings show.

The next energy level has the quantum number $n = 2$. There are $n^2 = 4$ different orbitals. For the hydrogen atom, these four orbitals have the same energy. One of the four is called the 2*s* orbital (two *s*). It has spherical symmetry. The 2*s* orbital, shown in Figure 9-7, is larger than the 1*s* orbital. The larger size seems reasonable because an electron in the 2*s* orbital has more energy than an electron in the

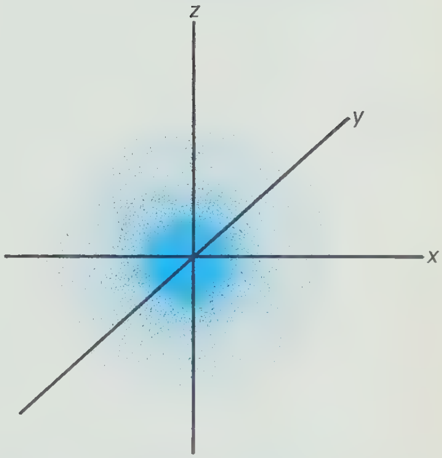


FIGURE 9-5

The 1*s* orbital for the hydrogen atom. An electron would be found in shaded region about 95% of the time.

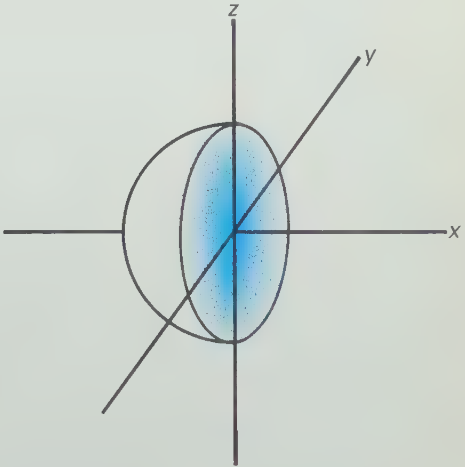


FIGURE 9-6

A cutaway view of the spherical 1*s* orbital.

1*s* orbital. The electron with higher energy is more likely to be found at a greater distance from the nucleus. For every value of *n*, there is one orbital with spherical symmetry. These orbitals are referred to as *s* orbitals. As *n* increases, these spherical orbitals are larger in size.

Now let us describe the other three orbitals for which $n = 2$. They are called 2*p* (two *p*) orbitals. These orbitals are not spherically symmetrical. For an electron in a *p* orbital, we are most likely to find the electron in two regions on opposite sides of the nucleus. The three 2*p* orbitals are shown in Figure 9-8. These orbitals lie along the *x*, *y*, and *z* axes. They are sometimes called $2p_x$, $2p_y$, and $2p_z$ orbitals to emphasize their directional character. Perhaps you can associate the letter *p* with the word "perpendicular" to help remember the directional properties of *p* orbitals. We shall see later that *p* orbitals are useful in explaining shapes of molecules. Every energy level with *n* greater than 1 has three *p* orbitals. As *n* increases, these *p* orbitals become larger in size. This means that on the average the electron has more energy and is farther from the nucleus if it is in a 3*p* orbital than in a 2*p* orbital.

When $n = 3$, there are $n^2 = 9$ orbitals. In the hydrogen atom, the nine orbitals have the same energy. There is one 3*s* orbital, three 3*p* orbitals, and five 3*d* orbitals. When $n = 4$, there are $n^2 = 16$ orbitals. There is one 4*s* orbital, three 4*p* orbitals, five 4*d* orbitals, and seven 4*f* orbitals. In this course we will not discuss *d* and *f* orbitals in any detail. Like the *p* orbitals, the *d* and *f* orbitals are not spherically symmetrical.

The energy level diagram for hydrogen is drawn in Figure 9-9. On the right side of this diagram, the orbitals for each energy level are shown as circles, ◯. This representation reminds us that an orbital corresponds to the space in which electrons are most likely to be found.

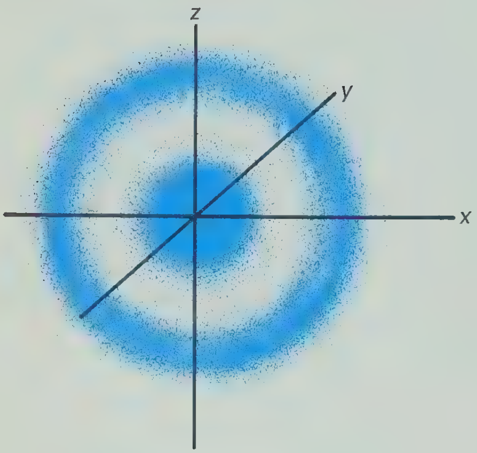
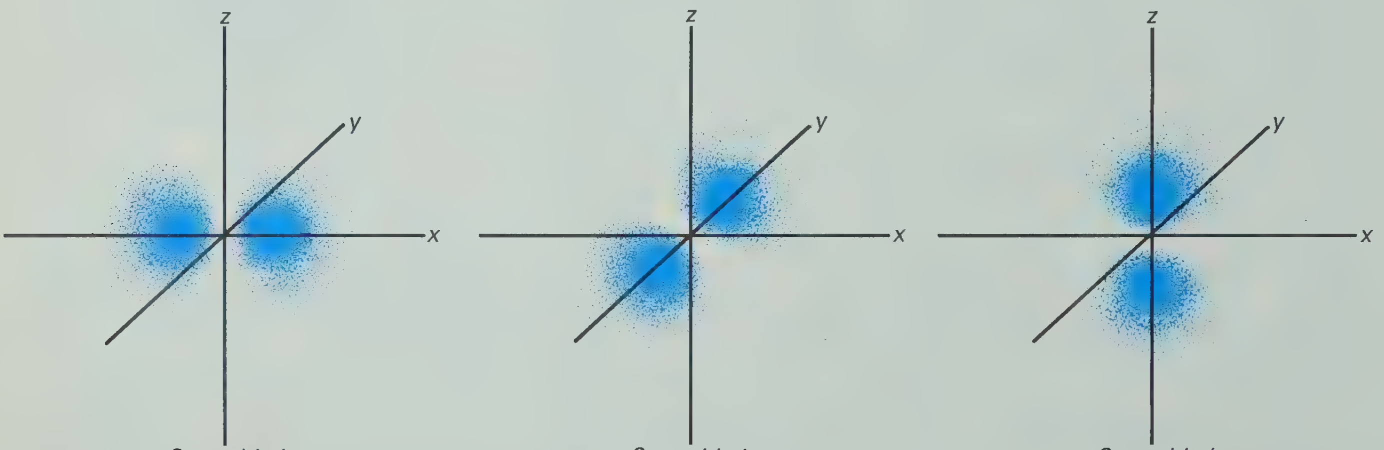


FIGURE 9-7

The 2*s* orbital for the hydrogen atom.



$2p_x$ orbital

$2p_y$ orbital

$2p_z$ orbital

FIGURE 9-8

The 2*p* orbitals for the hydrogen atom.

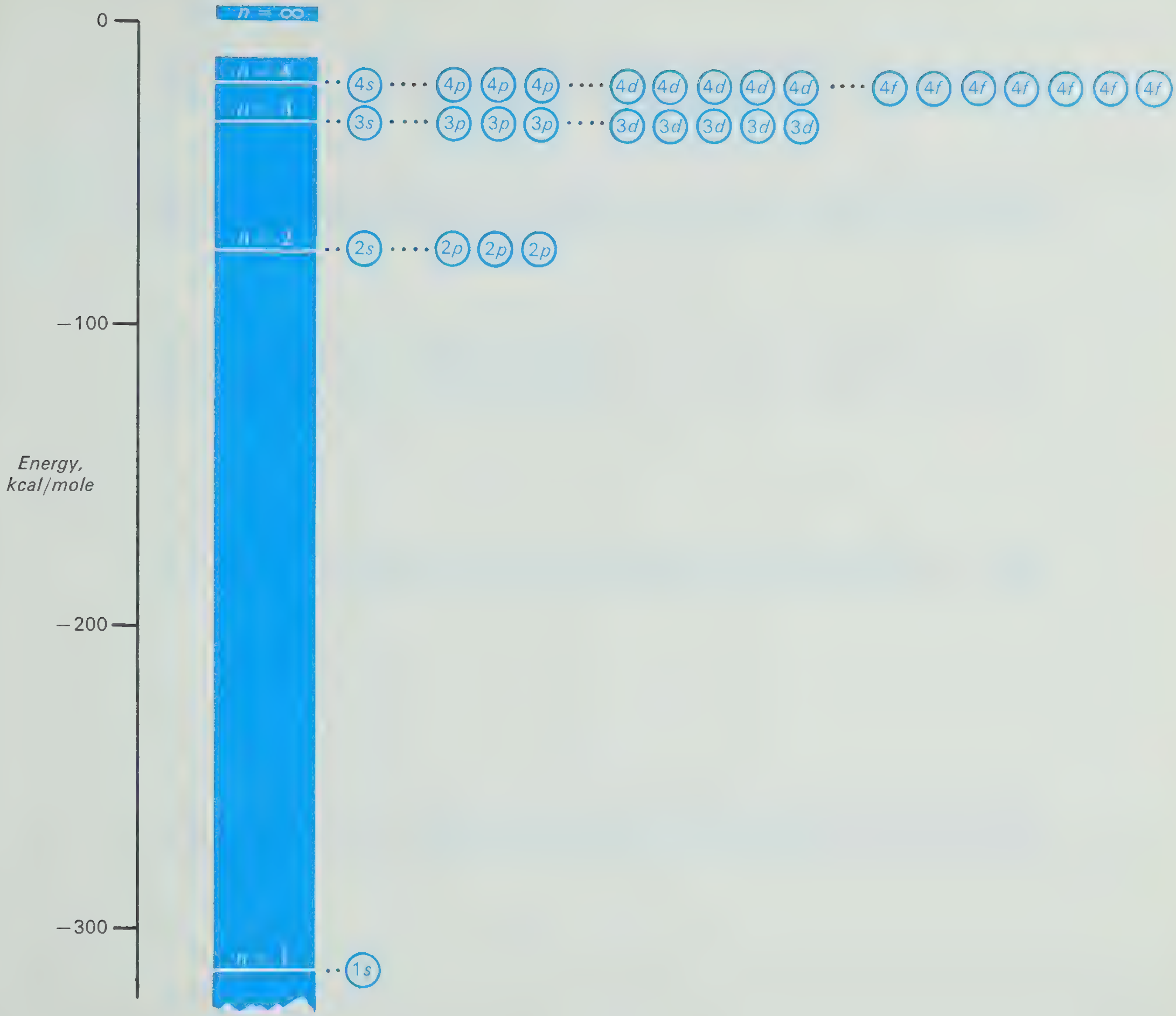

0
−100
−200
−300
Energy, kcal/mole
n = ∞
n = 4
n = 3
n = 2
n = 1
4s
4p
4p
4p
4d
4d
4d
4d
4d
4f
4f
4f
4f
4f
4f
4f
3s
3p
3p
3p
3d
3d
3d
3d
3d
2s
2p
2p
2p
1s

FIGURE 9-9

The energy level diagram for the hydrogen atom.

9-7 Orbitals for Atoms with More than One Electron

The line spectrum for hydrogen is the clue to the energy level diagram for the hydrogen atom. Gaseous samples of every element exhibit line spectra. However, most spectra are much more complex than the hydrogen spectrum shown in the figure on page 126. When these spectra are deciphered, we find that these regularities apply to all elements.

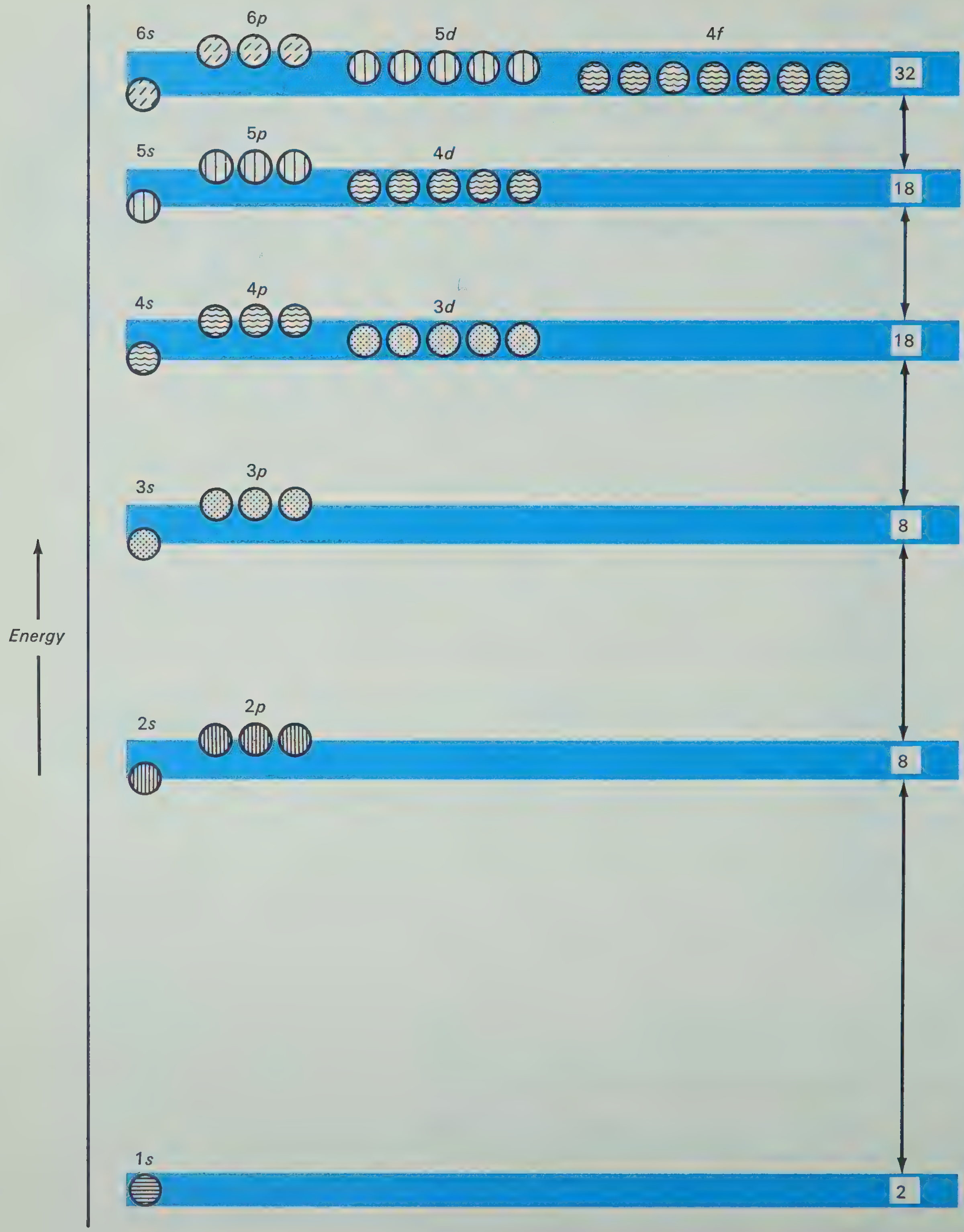

6s
6p
5d
4f
32
5s
5p
4d
18
4s
4p
3d
18
3s
3p
8
Energy
2s
2p
8
1s
2

FIGURE 9-10 A schematic energy level diagram for a many-electron atom.

Electrons can occupy only certain energy levels.

The observed spectral lines correspond to the
energy differences between these levels.

The energy level diagrams for elements with more than one electron are quite similar to the diagram for hydrogen. However, there are several important differences. For a particular value of the principal quantum number *n*, the n^2 orbitals in the hydrogen atom have the same energy. This is not true for any atom which has more than one electron. In these atoms the n^2 orbitals do not have the same energy. For example, the 2*p* orbitals have slightly higher energies than the 2*s* orbital. Figure 9-10, a schematic energy level diagram for all elements except hydrogen, will help you to see what happens. Compare this diagram with the one for hydrogen on page 149. Since the energy scale is different for each element, numerical values for energy have been omitted in this diagram. The effect of having more than one electron in an atom is a "tilting" of the orbital diagram. Try following the levels for $n = 3$ or 4 in Figure 9-10 to see the upward tilt. This tilt places the 3*d* orbitals at about the same energy as the 4*s* and 4*p* orbitals. Another consequence is shown by the numbers at the right side of this diagram. Remember we can place two electrons in each orbital. There is a large energy gap after we put two electrons in the 1*s* orbital. Another energy gap occurs after placing eight more electrons in the 2*s* and 2*p* orbitals. The large energy gaps occur after the accommodation of 2, 8, 8, 18, 18, 32 electrons. We saw those numbers in Table 9-2, page 146, when we talked about the noble gases. Now we can explain the Periodic Table in terms of orbitals. The electron configurations for the noble gases provide an important clue.

9-8 Orbitals and the Periodic Table

The energy levels for orbitals can help us understand the Periodic Table. We are going to build up the electron arrangement for the elements making use of Figure 9-10. The procedure to be followed is quite simple. We start with the hydrogen atom. It contains one proton in the nucleus and one electron in an orbital. The electron is accommodated in the lowest energy orbital, the 1*s* orbital.

The next element, helium, has two protons in the nucleus. Then two electrons must be in orbitals to provide electrical neutrality for the atom. Since an orbital can accommodate two electrons, both of the electrons for helium go into the 1*s* orbital. We say the electron arrangement in the helium atom is $1s^2$ (one *s* two). This is a shorthand way to show that there are two electrons in the 1*s* orbital. The notation $1s^2$ represents the arrangement of electrons and is called the **electron configuration.**

Some examples will help you to understand what happens. We will use the symbol ○ to represent any empty orbital. An orbital with one electron is indicated by ⦸ or by ⊘. Such an orbital is half filled. A filled orbital is shown with the symbol ⊗. By this

○ empty orbital

⦸ one electron
⊘ half fills an orbital

⊗ two electrons fill an orbital

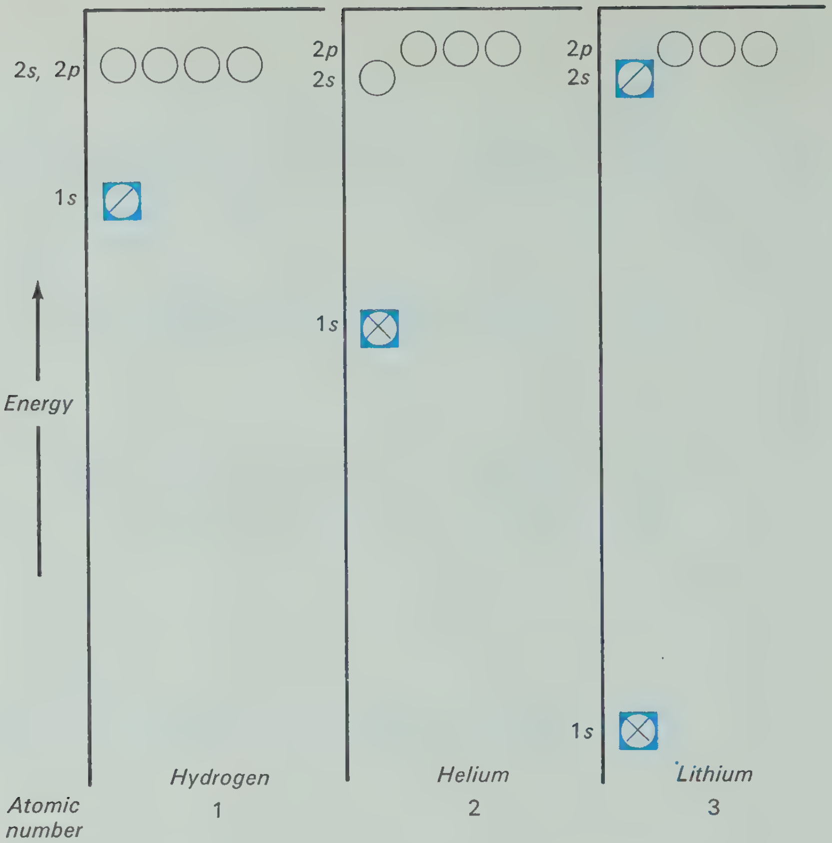


FIGURE 9-11

Schematic orbital diagrams for hydrogen, helium, and lithium atoms.

we mean there are two electrons in the orbital. Figure 9-11 shows the electron arrangements for the first three elements H, He, and Li. In the hydrogen atom, the single electron is in the lowest energy orbital, the 1*s*. In the helium atom, two electrons are in the 1*s* orbital.

For the next element, lithium, there are three protons in the nucleus. Two electrons occupy the 1*s* orbital. The third electron cannot enter this orbital because it is filled. The third electron must be placed in a higher energy orbital. The orbital of next higher energy is the 2*s*. The lithium atom has the electron configuration $1s^2\ 2s$ (one *s* two, two *s* one). The 2*s* electron in a lithium atom is weakly bound when compared to the 1*s* electrons. The 2*s* electron spends most of its time farther away from the nucleus than do the 1*s* electrons. It should be easy to remove the 2*s* electron to give the lithium ion, Li^+. In Section 7-3, page 111, we pointed out that the alkali metals readily form plus one ions. The energy diagram provides an explanation for this behavior.

Our schematic diagrams suggest that the electron in the 2*s* orbital of lithium is much farther away from the nucleus than the electron in the 1*s* orbital for hydrogen. But this is not true. To see why, let us look more closely at the electric forces in atoms.

As we construct electron configurations for atoms with high atomic numbers, we must assign electrons to orbitals that have large principal quantum numbers. We have to remember that the positive nuclear charge increases, too. Each electron in the atom experiences a much larger attractive force as the atomic number increases. These two effects just about balance each other. As the atomic number goes up, electrons must enter high energy orbitals. At the same time all electrons are pulled closer to the nucleus. The net result is that all atoms are approximately the same size.

The beryllium atom has four protons in the nucleus and four electrons in orbitals. Two electrons can occupy the 1*s* orbital and two can enter the 2*s* orbital. The electron configuration for a beryllium

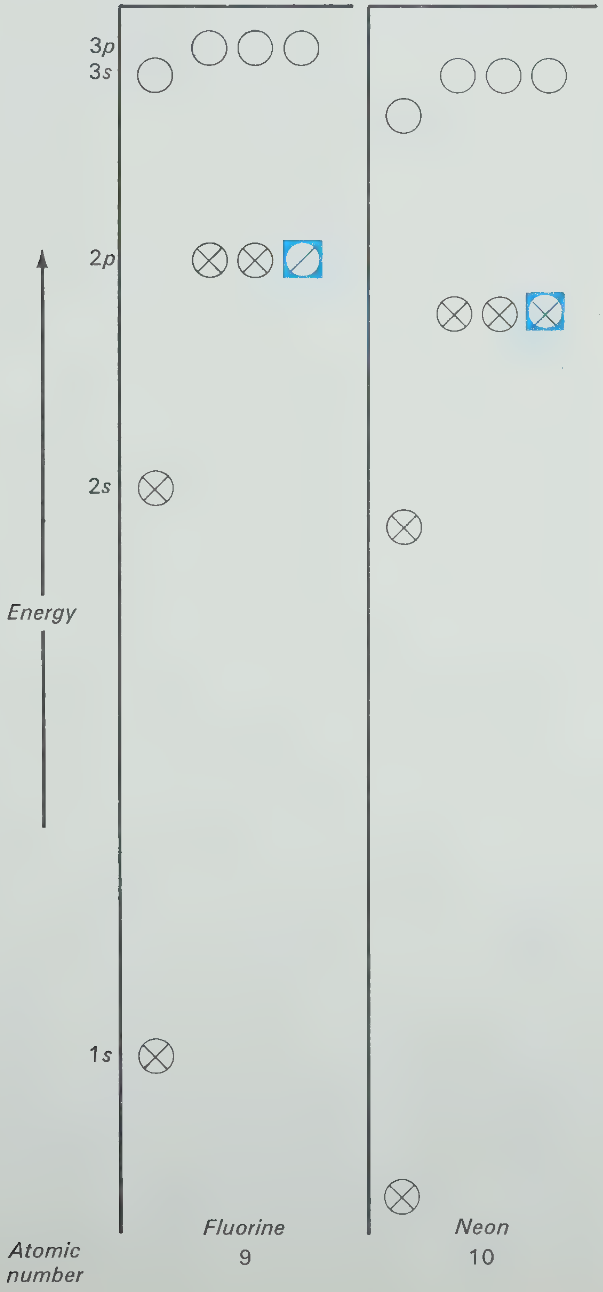


FIGURE 9-12

Schematic orbital diagrams for fluorine and neon atoms.

atom is $1s^22s^2$ (one *s* two, two *s* two). The 2*s* electrons will be most easily removed, forming the ion Be^{2+}.

The fifth electron, which is required for the next element boron, enters the lowest available orbital; one of the 2*p* orbitals. The electron configuration for boron can be written $1s^22s^22p$ (one *s* two, two *s* two, two *p* one). The pattern or regularity begins to develop.

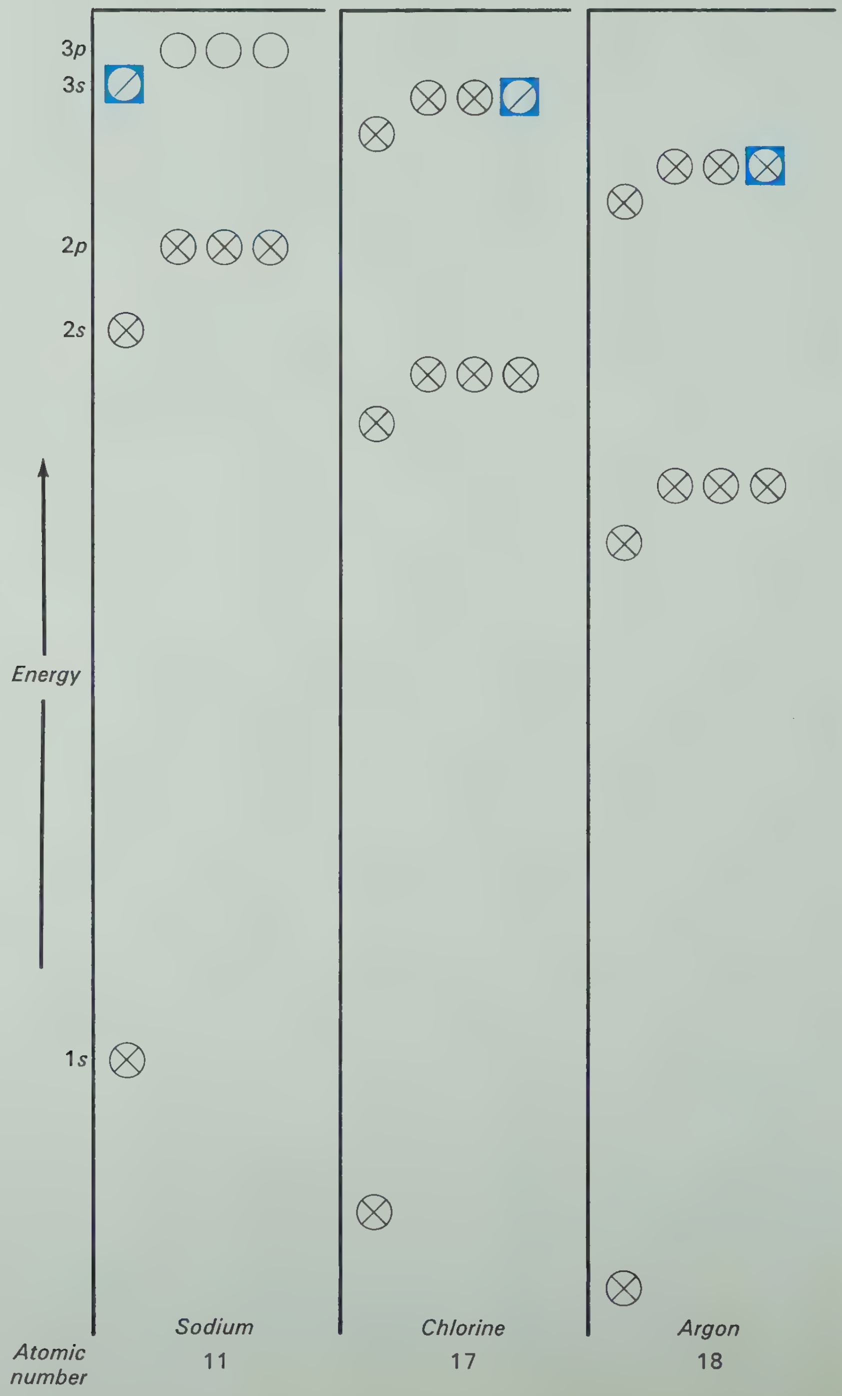

3p
3s
2p
2s
1s
Energy
Atomic number
Sodium
11
Chlorine
17
Argon
18

FIGURE 9-13

Schematic orbital diagrams for sodium, chlorine, and argon atoms.

Let us skip a few elements and discuss fluorine, the element with atomic number nine. Nine electrons must be placed in orbitals for the neutral atom of fluorine. The electron configuration $1s^2 2s^2 2p^5$ is shown in Figure 9-12. This notation is read: one *s* two, two *s* two, two *p* five. It means that the fluorine atom, in the lowest energy state, has two 1*s* electrons, two 2*s* electrons, and five 2*p* electrons for a total of nine electrons.

The next element neon has ten electrons. The last space in the 2*p* orbitals is filled for the Ne atom. This configuration is also shown in Figure 9-12. Table 9-3 summarizes what we have been saying.

TABLE 9-3

Electron Configurations for Atoms of the First Ten Elements

Element	Atomic Number	Electron Configuration
H	1	$1s$
He	2	$1s^2$
Li	3	$1s^2\ 2s$
Be	4	$1s^2\ 2s^2$
B	5	$1s^2\ 2s^2\ 2p$
C	6	$1s^2\ 2s^2\ 2p^2$
N	7	$1s^2\ 2s^2\ 2p^3$
O	8	$1s^2\ 2s^2\ 2p^4$
F	9	$1s^2\ 2s^2\ 2p^5$
Ne	10	$1s^2\ 2s^2\ 2p^6$

When we consider the next element, sodium, we encounter a situation similar to the one found for lithium. The eleventh electron for sodium must be in an orbital of higher energy, the 3*s* orbital. The lower energy orbitals are fully occupied. As we move to the elements chlorine and argon, we find that their electron configurations are very similar to those for fluorine and neon. Figure 9-13 shows the orbital configurations for sodium, chlorine, and argon.

9-9 Electron Configuration and the Periodic Table

You have probably recognized that there is an important regularity in the electron arrangements of the elements. This regularity is brought out in Figure 9-14. Each family of elements in the Periodic Table contains elements which have very similar electron arrangements.

In Chapter 7 we discussed three important families: the noble gases, the alkali metals, and the halogens. We can now look at each of these families in more detail. The noble gases He, Ne, and Ar have electron configurations that just fill the cluster of orbitals at a particular energy level. When orbitals are filled in this way, a particularly stable element is observed. The alkali metals and the halogens are elements with high chemical reactivity. Perhaps we

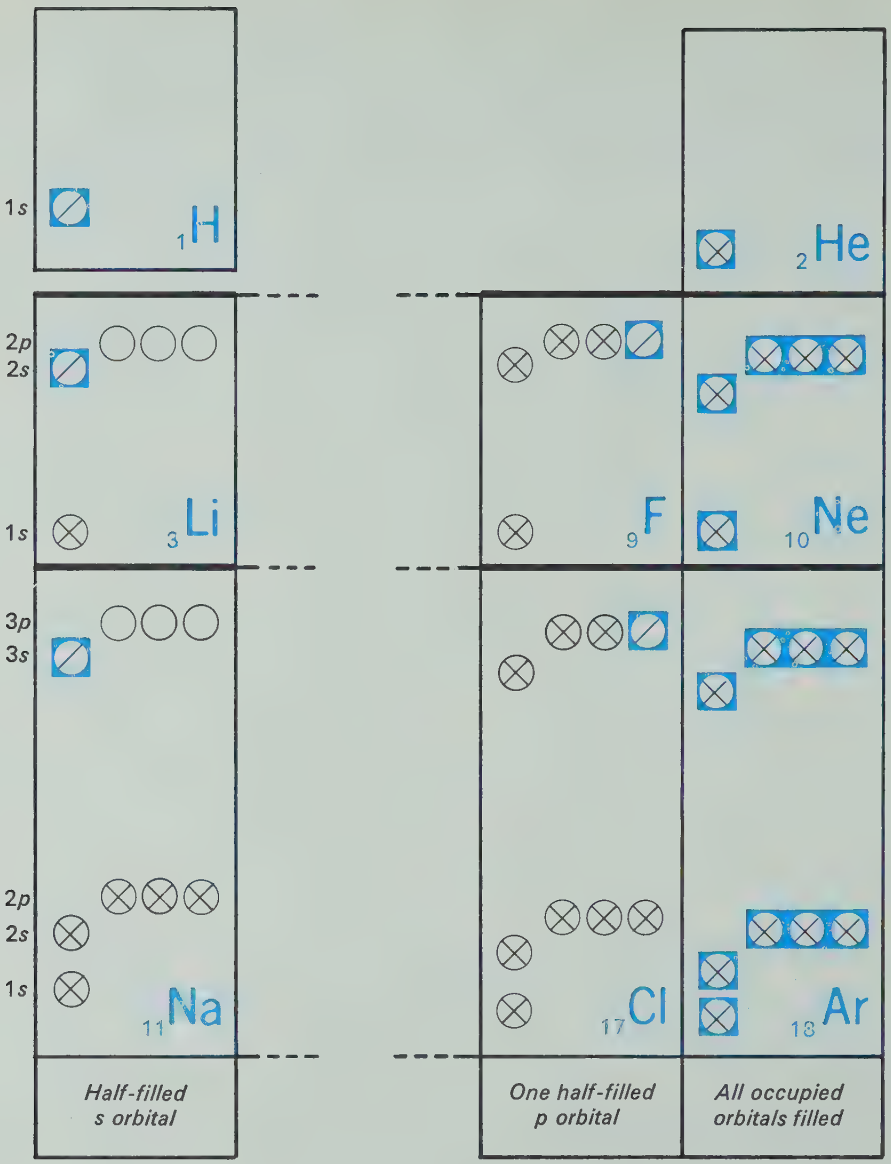

1s
$_1$H
$_2$He
2p
2s
1s
$_3$Li
$_9$F
$_{10}$Ne
3p
3s
2p
2s
1s
$_{11}$Na
$_{17}$Cl
$_{18}$Ar
Half-filled s orbital
One half-filled p orbital
All occupied orbitals filled

FIGURE 9-14

Regularity in electron arrangements in the Periodic Table.

can find an explanation for this difference of reactivity by looking at their electron configurations.

The alkali metals have electron configurations that place the electron with highest energy in an *s* orbital. A relatively small amount of energy is needed to remove this electron. An ion with charge 1+ forms. This ion has the same electron configuration as one of the noble gases. We can illustrate what happens with the following equations. The electron configuration is given below each species.

$$\mathrm{Li} \longrightarrow \mathrm{Li}^+$$

$1s^22s$ $\qquad$ $1s^2$ $\quad$ same electron configuration as He, $1s^2$

$\mathrm{Na} \longrightarrow \mathrm{Na^+}$

$1s^2 2s^2 2p^6 3s$ | $1s^2 2s^2 2p^6$ same electron configuration as Ne, $1s^2 2s^2 2p^6$

The chemical properties of the alkali metals result from the stable 1+ ions which have the same electron configurations as a noble gas.

The halogens, fluorine and chlorine, have configurations with one vacancy in the *p* orbitals. These elements readily accept one more electron from other elements to fill this vacant position. Ions with a 1− charge form. The ions take on the electron configuration of a noble gas.

$\mathrm{F} \longrightarrow \mathrm{F^-}$

$1s^2 2s^2 2p^5$ | $1s^2 2s^2 2p^6$ same electron configuration as Ne, $1s^2 2s^2 2p^6$

$\mathrm{Cl} \longrightarrow \mathrm{Cl^-}$

$1s^2 2s^2 2p^6 3s^2 3p^5$ | $1s^2 2s^2 2p^6 3s^2 3p^6$ same electron configuration as Ar, $1s^2 2s^2 2p^6 3s^2 3p^6$

The unusual stability of the electron configurations for the noble gases is an important point. The ions $\mathrm{Na^+}$ and $\mathrm{F^-}$ have the same electron configuration as Ne. We have hinted before that the noble gases provide an important clue to atomic structure. Energy level diagrams show clearly how sodium and fluorine form ions with the same electron arrangement as neon. The word **isoelectronic** means the same electron configuration. $\mathrm{Na^+}$, Ne, and $\mathrm{F^-}$ are isoelectronic.

Finally, let us look at hydrogen once more. It is placed in an isolated box in the Periodic Table. The electron configuration for hydrogen resembles those for lithium and sodium. Writing them in a column helps you to see that each has a single *s* electron in the highest occupied orbital.

Hydrogen		$1s$
Lithium	$1s^2$	$2s$
Sodium	$1s^2 2s^2 2p^6$	$3s$

On the other hand, the electron configuration for hydrogen also resembles those for fluorine and chlorine. Each of these atoms is one electron short of a noble gas structure.

H		$1s$		$1s^2$	He
F	$1s^2$	$2s^2 2p^5$	$1s^2$	$2s^2 2p^6$	Ne
Cl	$1s^2 2s^2 2p^6$	$3s^2 3p^5$	$1s^2 2s^2 2p^6$	$3s^2 3p^6$	Ar

Hydrogen is unusual among all the chemical elements. In some respects it is like an alkali metal. In other ways it is like a halogen.

9-10 Ionization Energy and the Periodic Table

We have referred to ionization energy in Chapter 7 in discussing the three chemical families: the noble gases, the alkali metals, and the halogens. Ionization of a neutral atom can be represented by the equation

$$\mathrm{M}(g) + \text{energy} \longrightarrow \mathrm{M}^+(g) + e^-$$

Orbital diagrams will help us understand what happens. The ionization of lithium is shown in Figure 9-15. The ionization energy, 124 kcal/mole, is just sufficient to raise the 2*s* electron to the energy level, $n = \infty$.

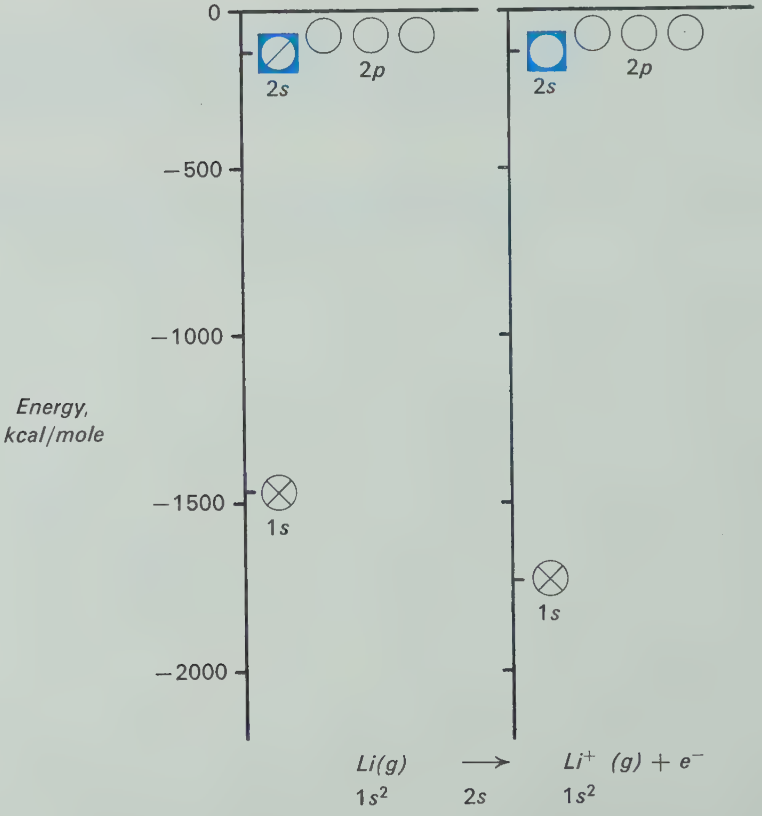


FIGURE 9-15

Ionization of lithium.

Many systematic determinations of ionization energies were carried out in the decade after Bohr proposed his atomic model. The first measurements were made by bombarding an atomic vapor with high energy electrons. In this method the energy of the electrons was known very precisely. When the kinetic energy of the bombarding electron is increased slowly, a critical value is reached at which positive ions can be detected electrically. These ions result from interactions between atoms and bombarding electrons that have been given just enough kinetic energy to cause the most weakly bound electron to be ejected from the atom. This critical value is found to be characteristic of the substance being investigated. The ionization energies for the first twenty elements are listed in Table 9-4.

TABLE 9-4

Ionization Energy for Some Elements

Atomic Number	Element	Ionization Energy (kcal/mole)
1	H	313.6
2	He	566.7
3	Li	124.3
4	Be	214.9
5	B	191.2
6	C	259.5
7	N	335
8	O	313.8
9	F	401.5
10	Ne	497
11	Na	118.4
12	Mg	175.2
13	Al	137.9
14	Si	187.9
15	P	241.7
16	S	238.8
17	Cl	300
18	Ar	363.2
19	K	100
20	Ca	141

A number of regularities become apparent when these values are shown in graphical form, Figure 9-16.

First, there is a gradual increase in ionization energy as we move across a row of the Periodic Table. The noble gas element has the highest ionization energy of the elements in a particular row. Second, there is a sharp decrease in ionization energy as we proceed from a noble gas to the next element, an alkali metal. There is a striking similarity between the ionization energies and the periodicity of chemical properties. This is not accidental. We shall see that many trends in chemical properties can be explained in terms of trends in ionization energies.

It is possible to remove more than one electron from a many-electron atom. Of course, more energy is always required to remove the second electron than to remove the first. The second electron has to leave an ion which already has a net positive electric charge. The values of successive ionization energies are important to chemists.

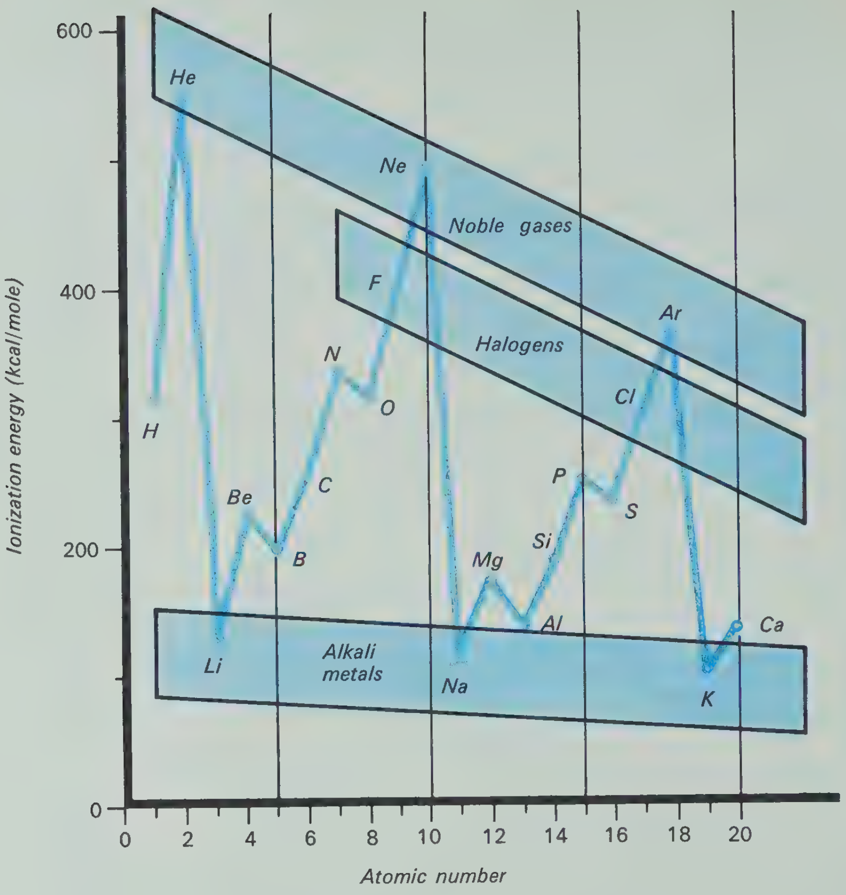


FIGURE 9-16

Ionization energies for the first twenty elements.

Look at the ionization energy of the first three elements — helium, lithium, and beryllium. The first, second, and third ionization energies are given in Table 9-5. These energies correspond to the reactions:

$$M(g) + IE_1 \longrightarrow M^+(g) + e^-$$
$$M^+(g) + IE_2 \longrightarrow M^{2+}(g) + e^-$$
$$M^{2+}(g) + IE_3 \longrightarrow M^{3+}(g) + e^-$$

TABLE 9-5

Successive Ionization Energies in kcal/mole

Element	Electron Configuration of Element	IE_1	IE_2	IE_3
He	$1s^2$	567	1254	–
Li	$1s^2\ 2s$	124	1744	2823
Be	$1s^2\ 2s^2$	215	420	3548

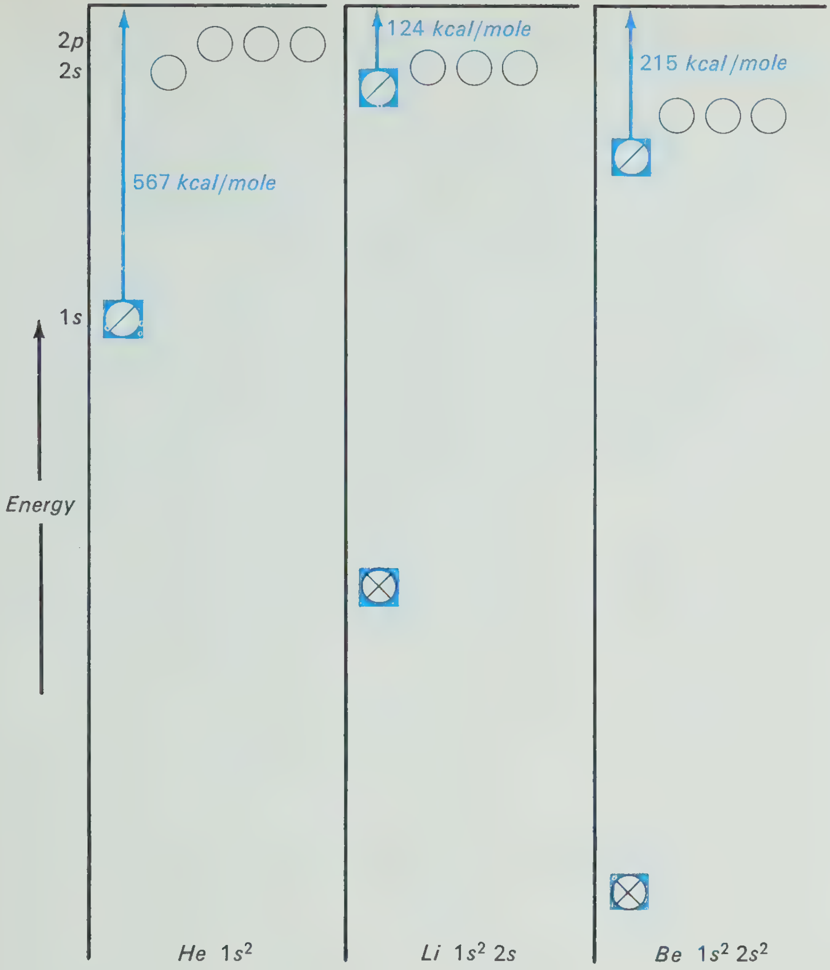


FIGURE 9-17

First ionization energy, energy required to remove an electron from He, Li, and Be atoms.

We can understand the relative size of the ionization energies by comparing the energy level diagrams for these three elements. A very large amount of energy is necessary to ionize He. We do not expect He^+ to form readily. A much smaller amount of energy is needed to ionize Li or Be. The ions Li^+ and Be^+ form readily.

Let us see what the energy level diagram is like for removing the second electron from each of these ions. This is shown in Figure 9-18.

The energy required to form He^{2+} or Li^{2+} is very large. We do not expect these ions to form readily. However, for beryllium, only a moderate amount of energy is needed to remove the second electron. The formation of Be^{2+} is reasonable. The explanation lies in the fact that formation of Be^{2+} removes electrons from the 2*s* orbital. For Li^{2+}, the second electron comes from the 1*s* orbital. The 1*s* orbital is much further below $n = \infty$ than the 2*s* orbital.

The electrons that are easily removed from an element establish the chemical properties of that element. Chemists call these the **valence electrons** for the element. The number of electrons in *s* and *p* orbitals, beyond a noble gas structure, will be called valence electrons.* The number of valence electrons in He, Li, and Be are 0, 1, and 2, respectively.

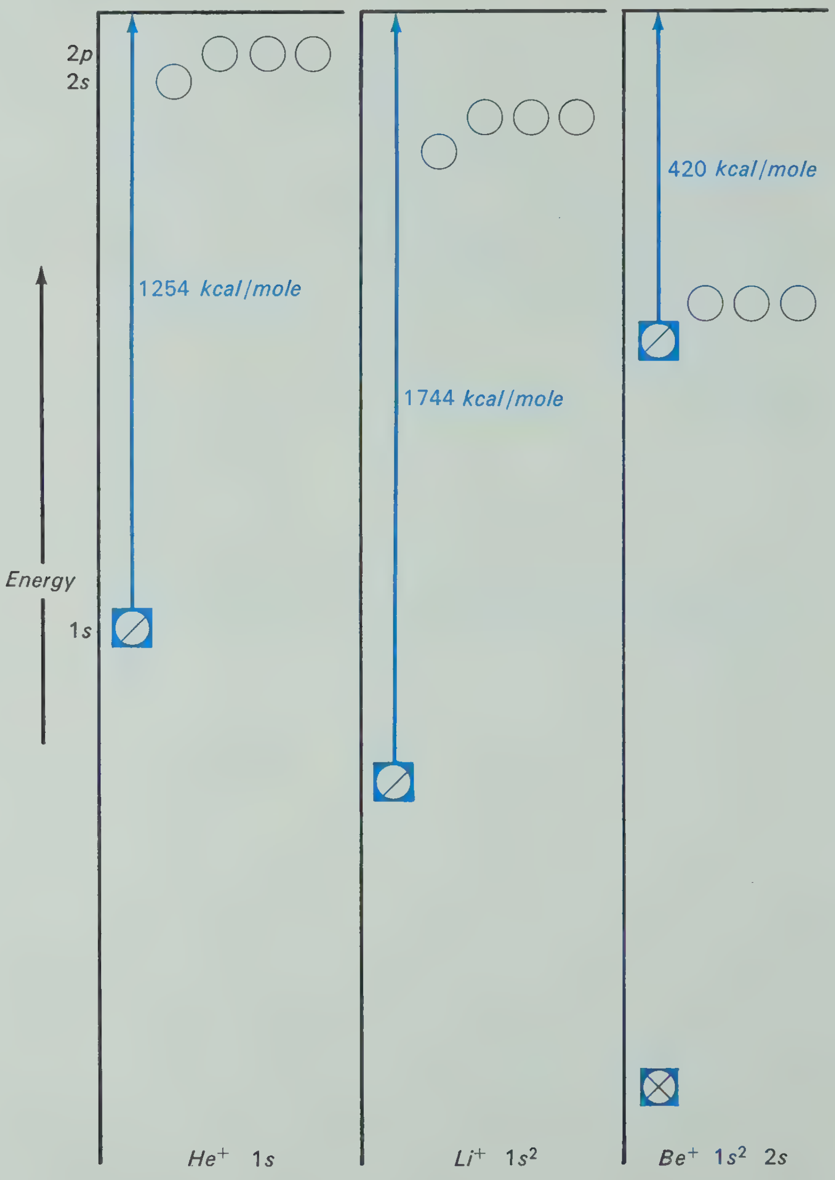

2p
2s
1s
Energy
1254 kcal/mole
1744 kcal/mole
420 kcal/mole
He+ 1s
Li+ 1s2
Be+ 1s2 2s

FIGURE 9-18

Second ionization energy, energy required to remove an electron from He$^+$, Li$^+$, and Be$^+$ ions.

9-11 The Fourth Row of the Periodic Table

We will finish this chapter by discussing the electron configurations for elements beyond argon. Look back at the schematic orbital diagram given in Figure 9-10. The 3*p* orbitals are filled at argon. The next cluster of orbitals must be those with about the same energy as the 4*s* orbital. We see that something new happens. There are nine orbitals with about the same energy: the 4*s* orbital, three

---

* We will want to modify this statement in Chapter 20.

4*p* orbitals, and five 3*d* orbitals. This row in the Periodic Table is different from the second and third rows. There are eighteen elements in the fourth row instead of eight elements.

Potassium and calcium have electron configurations which place them in the families headed by lithium and beryllium.

K	$1s^2$	$2s^22p^6$	$3s^23p^6$	$4s$
Ca	$1s^2$	$2s^22p^6$	$3s^23p^6$	$4s^2$

When we consider the next element, scandium, the 21st electron will be placed in the available orbital of lowest energy. The 3*d* orbitals happen to be slightly lower in energy than the 4*p* orbitals. Consequently the electron configurations for the next ten elements, scandium through zinc, show electrons in 3*d* orbitals. These elements are called **transition elements.** We will discuss some of their chemical properties in Chapter 20.

After the 3*d* orbitals are filled, the next orbitals to fill are the 4*p* orbitals. Let us write the configuration for gallium in a way to stress its direct relation with boron and aluminum. We have moved the $3d^{10}$ configuration ahead of $4s^2$ and 4*p* for convenience.

Ga $1s^2$ $2s^22p^6$ $3s^23p^6$ $3d^{10}\ 4s^24p$

EXERCISE 9-3

Write the electron configurations of aluminum and boron. In what way are they related to that for gallium?

The remaining elements in this row add 4*p* electrons until the noble gas krypton is reached.

Kr $1s^2$ $2s^22p^6$ $3s^23p^6$ $3d^{10}4s^24p^6$

Instead of eight elements forming the fourth row, there are eighteen because the 3*d* orbitals have energies about the same as the 4*s* and 4*p* orbitals.

The same pattern of eighteen elements is found for the fifth row of the Periodic Table. The 4*d* orbitals have energy close to the 5*s* and 5*p* orbitals. The ten transition elements, yttrium through cadmium, appear immediately under scandium through zinc. As usual, another noble gas, xenon, appears when the 5*p* orbitals are filled.

The sixth row of the Periodic Table presents something new once more. Here, four kinds of orbitals are involved that have about the same energy: 6*s*, 5*d*, 4*f*, and 6*p*. After two electrons are put in the 6*s* orbital and one is put in the 5*d* orbital, the next fourteen electrons go into the seven 4*f* orbitals. This series of fourteen elements is called the **rare earth elements.** Their chemical properties are so similar that for many years it was very difficult to separate these elements from each other. In the last twenty years, methods have been developed to achieve separation of the rare earth elements.

We will not pursue this discussion further. The number of elements in each row of the Periodic Table can be associated with the clustering of orbitals at approximately the same energy level. Table 9-6 summarizes this information.

TABLE 9-6

The Number of Elements in Each Row of the Periodic Table

Row	Number of Elements	Orbitals Being Filled for Each Row
1	2	1*s*
2	8	2*s* 2*p*
3	8	3*s* 3*p*
4	18	4*s* 3*d* 4*p*
5	18	5*s* 4*d* 5*p*
6	32	6*s* 4*f* 5*d* 6*p*
7	(32)	7*s* 5*f* (6*d* 7*p*)

9-12 Review

Niels Bohr proposed an atomic model which can be compared with our solar system. The nucleus of the atom corresponds to the sun. Electrons moving in specific orbits around the nucleus are like the planets. This model was the first to offer an explanation for the line spectrum of hydrogen. The Bohr model was based on the idea that the atom can only exist in certain energy states. Changes from one state to another must be accompanied by absorption or emission of energy. *One can think of these transitions in terms of an energy staircase.*

Important as this model was, it has been replaced by the quantum mechanical model for the atom. Bohr's planetary orbits for the electron have been replaced by *orbitals.* Orbitals are regions of space *in which electrons are most likely to be found.* Orbitals have size and shape, and each orbital can accommodate up to two electrons. Transition from one orbital to another is accompanied by a specific energy change.

The orbital model for the atom offers an explanation for the arrangement of the chemical elements in the Periodic Table. There is a natural grouping of elements into chemical families on the basis of similar electron configurations.

The number of elements in a row of the Periodic Table is explained in terms of groupings of orbitals with approximately the same energy. The elements called the **noble gases** occur just as these groups of orbitals are fully occupied. The next set of orbitals is considerably higher in energy. The great chemical stability of the noble gases can be correlated with their electron configuration.

The elements with one electron less than a noble gas are called the **halogens.** The elements with one electron more than a noble gas are called the **alkali metals.** These families have very high chemical activity. They exhibit a great tendency to form ions that have the same electron configuration as a noble gas.

The chemical properties for each family of elements can be related to the electron configuration characteristic of that family. The electrons in the highest energy orbitals for any particular element are always the easiest electrons to remove. Chemists call these the **valence electrons** of the element. The valence electrons establish the chemical properties of each element.

Questions and Problems for Chapter 9

1

Use the energy level diagram in Figure 9-4 to calculate the energy required to raise the electron in a hydrogen atom from level $n = 1$ to each of the higher energy levels. Compare these energies with the spectral lines shown in the figure on p. 126.

2

Repeat Problem 9-1, using level $n = 2$ for the starting level.

3

Determine the value of E_n for $n = 1, 2, 3, 4$, for a hydrogen atom using the relation $E_n = -313.6/n^2$.

4

The first ionization energy for lithium is 124 kcal/mole. Determine the frequency for one possible line in the lithium emission spectrum. In what part of the spectrum would the line appear? $E = h\nu$, $h = 9.52 \times 10^{-14}$ kcal sec/mole. Refer to the upper figure on p. 125.

5

According to the quantum mechanical description of the 1*s* orbital of the hydrogen atom, what relation exists between the surface of a sphere centered about the nucleus and the location of an electron?

6

What must be done to a 2*s* electron to make it a 3*s* electron? What happens when a 3*s* electron becomes a 2*s* electron?

7

The quantum mechanical description of the 1*s* orbital is similar in some respects to a description of the holes in a much used dartboard. For example, the "density" of dart holes is constant anywhere on a circle centered about the bull's-eye, and the "density" of dartholes reaches zero only at a very long distance from the bull's-eye. What are the corresponding properties of a 1*s* orbital?

In the light of your answer, point out erroneous features of the following models of a hydrogen atom (both of which were used before quantum mechanics demonstrated their inadequacies).

(a) A ball of uniform density.
(b) A "solar system" atom with the electron circling the nucleus at a fixed distance.

8

Make a table listing the principal quantum numbers (through three), the types of orbitals, and the number of orbitals of each type.

9

Name the elements that correspond to each of the following electron configurations:

$1s^2$
$1s^2 \quad 2s^1$
$1s^2 \quad 2s^22p^1$
$1s^2 \quad 2s^22p^3$
$1s^2 \quad 2s^22p^6 \quad 3s^23p^6 \quad 4s^1$

10

Consider these two electron populations for neutral atoms:

A. $1s^2$ $2s^22p^6$ $3s^1$;
B. $1s^2$ $2s^22p^6$ $6s^1$.

Which of the following is FALSE?

(a) Energy is required to change A to B.
(b) A represents a sodium atom.
(c) A and B represent different elements.
(d) Less energy is required to move one electron from B than from A.

11

Name the atoms whose orbital occupancy corresponds to those listed below. Assume all lower energy orbitals to be full and the atom to be in its lowest energy state.

(a) $2s^1$
(b) $3p^4$
(c) $3s^1$
(d) $3p^6$
(e) $4p^1$
(f) $2p^1$
(g) $1s^2$
(h) $6s^1$
(i) $5p^5$

12

Write the orbital occupancy for the elements indicated. Refer to the orbital diagram, Figure 9-9.

(a) element with atomic number 9
(b) element with atomic number 13
(c) element with atomic number 20
(d) element with atomic number 7

13

The electron configuration for lithium is $1s^22s^1$ and for beryllium it is $1s^22s^2$. Without referring back to Figures 9-16 and 9-17, estimate the approximate ionization energies to remove first one, then a second, electron. Explain your estimates.

14

Which of the following electron configurations would you expect to have the lowest second ionization energy? Give reasons for your choice.

(a) $1s^22s^22p^6$
(b) $1s^22s^22p^63s^1$
(c) $1s^22s^22p^63s^2$

15

The first four ionization energies of boron atoms are as follows:

E_1 = 191 kcal/mole
E_2 = 578
E_3 = 872
E_4 = 5962

Explain the magnitudes in terms of the electron configuration of boron and deduce the number of valence electrons of boron.

16

How many valence electrons has carbon? Silicon? Phosphorus? Hydrogen? Write the electron configuration for a neutral atom of each element.

17

How many valence electrons has radium? Barium? Bromine? Bismuth? (Count only *s* and *p* electrons.) Write the valence electron configuration for a neutral atom of each element.

18

Write the orbital description for the *valence* electrons of each element in

(a) column 1 of the Periodic Table
(b) column 2
(c) column 6
(d) column 7

Chemical Bonding

10

In the last chapter we saw how the orbital model leads to the electron configurations of the atoms. In this chapter we want to see how the orbital model can be applied to molecules. Chemists are concerned primarily with molecules, not atoms.

Some atomic arrangements stay together long enough for us to measure the chemical and physical properties of the entire cluster. We use the word molecule to refer to the atomic cluster. For some molecules we have to act fast if we hope to measure their properties. Molecules such as OH and CH_3 have very high chemical activity. They react in a fraction of a second. Many molecules are like H_2O and CH_4. Their chemical activity is relatively low at room temperature. We do not have to hurry to measure their properties.

Chemists recognize that electric forces hold atoms together in molecules. When all the electric forces (some attractive and some repulsive) between two atoms are summed up, a molecule forms if the electric attractions are stronger than the electric repulsions. Chemists then say that a **chemical bond** forms between two atoms. An understanding of the nature of a chemical bond is one of the chemist's major goals. After all, think what happens in a chemical reaction. The number of atoms does not change, but the arrangement of bonds between atoms does change. Some chemical bonds disappear. New chemical bonds form. Our ideas of chemical bonding should provide answers to questions like these.

> Why are only certain chemical formulas found? Why is hydrogen H_2, instead of H_3?
>
> Why do some molecules such as OH show very high chemical activity while molecules such as H_2O do not?
>
> Why do molecules have different shapes? BF_3 is a flat or planar molecule. NF_3 has the shape of a pyramid.
>
> Why do chemical bonds form at all?

This last question is perhaps the most important, yet in certain ways it is the easiest question to answer. A chemical bond forms between two atoms because electrons are attracted simultaneously to both atomic nuclei. We can represent what we are saying with orbital drawings. If a chemical bond forms between atoms *A* and *B*, then the probability of finding electrons in the region between the two nuclei is very high.

$$A + B \longrightarrow AB$$

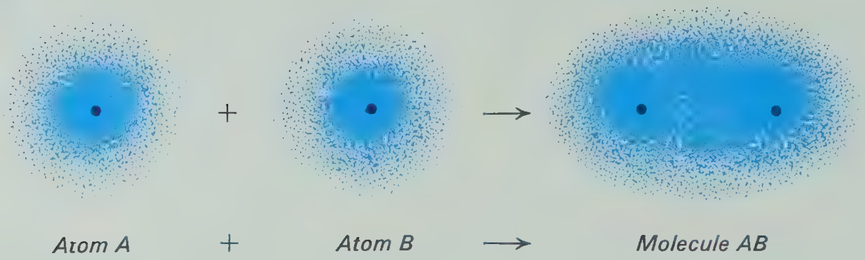


FIGURE 10-1

Electron distribution in stable molecule *AB*.

If a chemical bond does not form between atoms *X* and *Y*, then the probability of finding electrons in the region between the two nuclei is very low.

$$X + Y \longleftarrow XY$$

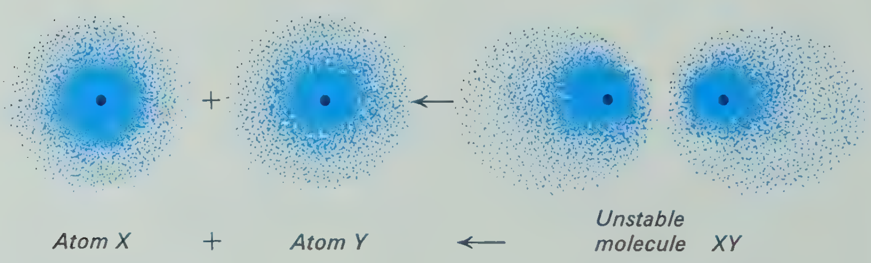


FIGURE 10-2

Electron distribution in unstable molecule *XY*.

Our discussion of chemical bonding will be in two parts. First we will discuss ionic bonding and then, covalent bonding. The language used by chemists makes it appear that these bonds are entirely different. Before we finish this chapter, we will see that all chemical bonds originate in the same way.

10-1 Ionic Bonding

We talked about the reaction of metallic sodium with chlorine gas in Section 7-3, page 114. The product, sodium chloride, is a white crystalline solid. The crystal is built up of positive ions, Na^+, alternating with negative ions, Cl^-.

$$2\,Na(s) + Cl_2(g) \longrightarrow 2\,Na^+Cl^-(s)$$

Solids such as sodium chloride are called **ionic solids.** We use the words **ionic bonds** to describe the bonding in ionic solids. Table 10-1 lists some of the general properties for substances with ionic bonding.

TABLE 10-1

Some Properties of Ionic Solids

Observed Property	Interpretation
High melting temperatures.	Strong forces hold particles together in the solid.
When molten, good conductors of electricity.	Ions are present in molten state.
If soluble in water, solutions are good conductors of electricity.	Ions are present in aqueous solutions.

Our model for ionic bonding is a very simple one. When sodium reacts with chlorine, ions with opposite electric charge form during the chemical reaction. The stability of an ionic solid arises primarily because of electrostatic interactions between the ions. Ions with opposite electric charge attract each other, and energy is needed to separate them.

⊕⊖ plus energy ⟶ ⊕ plus ⊖

The potential energy of the system is smaller when the ions are close together. What happens if a third ion enters this system?

⊕⊖ plus ⊕ ⟶ ⊕⊖⊕ plus energy

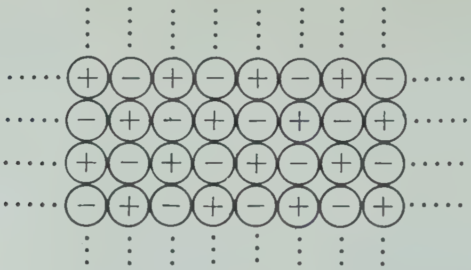
We can convince ourselves that the arrangement on the right of the arrow has less potential energy than the one on the left by considering the forces in this set of three ions. There are now two attractive forces, one between each positive ion and the negative ion. In addition, there is one repulsive force between the two positive ions. However, the positive ions are farther apart than either positive-negative pair. The repulsive force is not as large as the second attractive force in this three ion arrangement.

⊕⊖⊕ has less potential energy
than ⊕⊖ or ⊕⊖ plus ⊕.

We can continue to let our "crystal" grow in one dimension. Attractive and repulsive forces come into play as each ion is added. But the new attractive forces are always greater than the new repulsive forces. The ionic crystal grows. The potential energy continues to decrease. In one dimension the crystal looks like this.

. . . ⊕⊖⊕⊖⊕⊖⊕⊖⊕⊖⊕ . . .

In two dimensions the crystal can be drawn like this.



The larger the crystal, the lower the potential energy of the system. It is easy to understand why ionic crystals grow large enough to be seen.

Let us return to the orbital model for the atom. Does an understanding of orbitals help us to understand ionic bonding? Can we predict the electric charge on ions? A look at the example Na^+Cl^- will show how the orbital model guides us. The important clue is the great chemical stability of the noble gases.

Table 10-2 shows the electron configurations for the elements sodium and chlorine. When these elements react, each sodium atom gives up an electron; each chlorine atom gains an electron. The ions that form have the same electron configurations as the noble gases neon and argon.

TABLE 10-2

The Electron Configurations in the Sodium-Chlorine Reaction

Reaction				Noble Gas Isoelectronic with Ion
Na $1s^22s^22p^63s$		$\longrightarrow$	Na^+ $1s^22s^22p^6$	Ne $1s^22s^22p^6$
			$+ e^-$	
Cl $1s^22s^22p^63s^23p^5$	$+ e^-$	$\longrightarrow$	Cl^- $1s^22s^22p^63s^23p^6$	Ar $1s^22s^22p^63s^23p^6$

An important generalization is suggested by this example.

> Ionic bonding occurs when elements gain and lose electrons to form ions.
>
> The electron configuration for each ion is the same as that for a noble gas.

We can test this generalization by looking at some other substances. We know that each of the alkali metals forms an ionic solid with each halogen. The formula for each of these solids can be represented as M^+X^-. Look at Tables 10-3 and 10-4. Electron configurations for various ions are compared with the noble gas electron arrangements. All of the alkali halides are in agreement with our generalization.

TABLE 10-3

Electron Configurations for Some of the
Alkali Elements and Their Ions

Element	Ion	Noble Gas Isoelectronic with Ion
Li $1s^22s$	Li^+ $1s^2$	He $1s^2$
Na $1s^22s^22p^63s$	Na^+ $1s^22s^22p^6$	Ne $1s^22s^22p^6$
K $1s^22s^22p^63s^23p^64s$	K^+ $1s^22s^22p^63s^23p^6$	Ar $1s^22s^22p^63s^23p^6$

TABLE 10-4

Electron Configurations for Some of the
Halogens and Their Ions

Element	Ion	Noble Gas Isoelectronic with Ion
F $1s^22s^22p^5$	F^- $1s^22s^22p^6$	Ne $1s^22s^22p^6$
Cl $1s^22s^22p^63s^23p^5$	Cl^- $1s^22s^22p^63s^23p^6$	Ar $1s^22s^22p^63s^23p^6$

What do we find when we consider other families of elements? Let us look at the elements in the second and sixth columns of the Periodic Table. The alkaline earth metals, Be through Ra, form ions with a 2+ charge. The elements O through Te form negative ions with a 2− charge. These elements form compounds with the general formula MX. Table 10-5 compares electron configurations for some of the elements in these families.

TABLE 10-5

Electron Configurations for Some Elements of the
Alkaline Earth and Oxygen Families, and Their Ions

Element	Ion	Noble Gas Isoelectronic with Ion
Be $1s^22s^2$	Be^{2+} $1s^2$	He $1s^2$
Mg $1s^22s^22p^63s^2$	Mg^{2+} $1s^22s^22p^6$	Ne $1s^22s^22p^6$
O $1s^22s^22p^4$	O^{2-} $1s^22s^22p^6$	Ne $1s^22s^22p^6$
S $1s^22s^22p^63s^23p^4$	S^{2-} $1s^22s^22p^63s^23p^6$	Ar $1s^22s^22p^63s^23p^6$

We see an immediate explanation for the formula MX. Electrical neutrality is achieved when one ion with charge 2+ and one with charge 2− combine. Several examples illustrate the ionic nature of these compounds. Electrical neutrality can be readily seen.

$$Be^{2+}O^{2-} \qquad Mg^{2+}O^{2-} \qquad Mg^{2+}S^{2-}$$

Each ion has the electron configuration of a noble gas element.

What type of formula is expected when beryllium reacts with chlorine or sodium with oxygen? We already know the ions each element forms. The only additional requirement in writing an empirical formula is to achieve electrical neutrality. Write the formulas in expanded form first.

$$Be^{2+} + Cl^- + Cl^- \longrightarrow BeCl_2$$
$$Na^+ + Na^+ + O^{2-} \longrightarrow Na_2O$$

The second generalization under Table 10-2 is helpful. The electron configuration of an element guides us to the type of ion it forms. The requirement of electrical neutrality then guides us in writing the empirical formula of an ionic compound.

EXERCISE 10-1

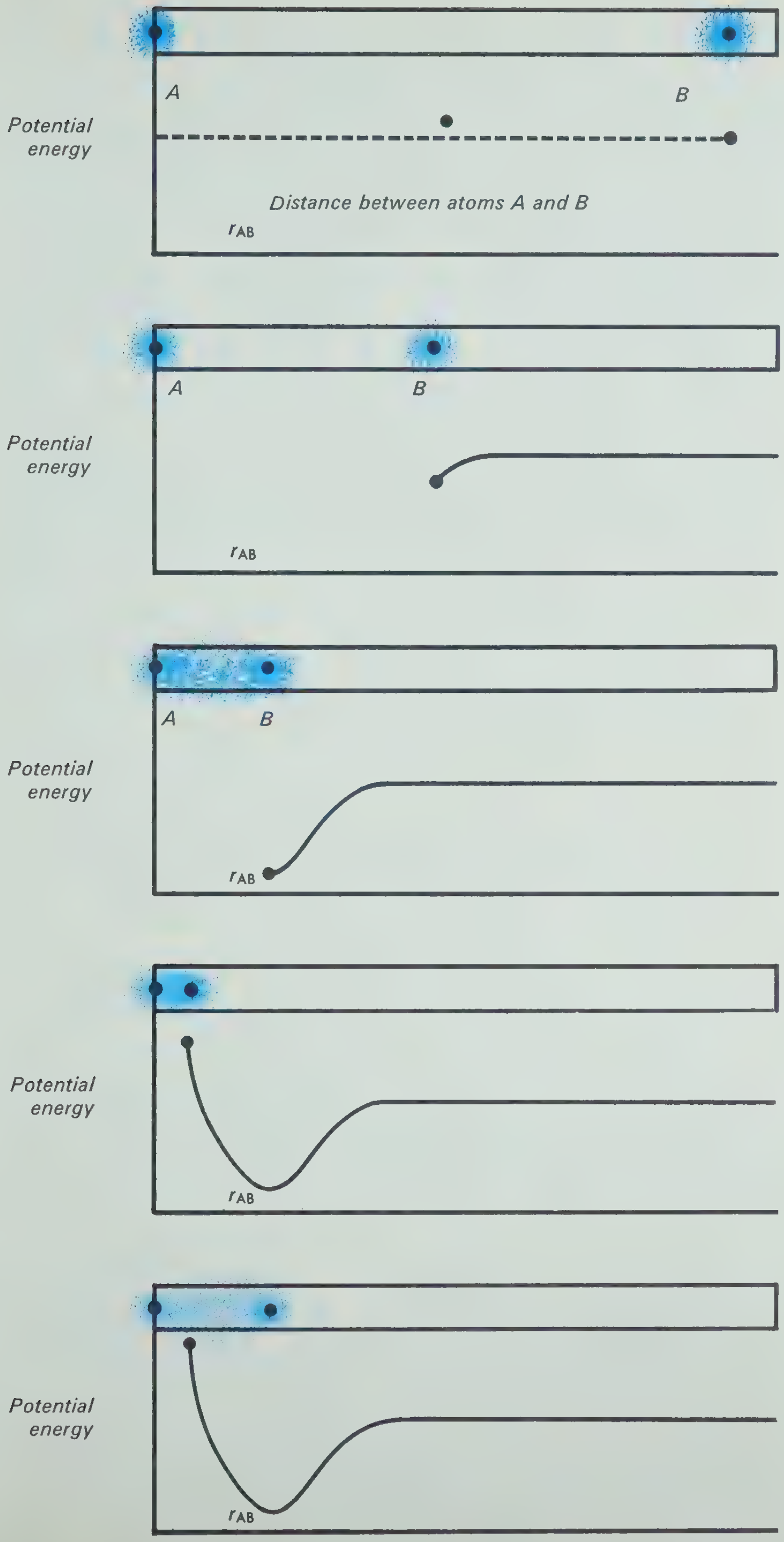
Write out the electron configuration for Al. If aluminum forms an ion, what would you expect its electric charge to be? What formula would you expect if aluminum and oxygen form an ionic compound?

10-2 Covalent Bonding

In the introduction to this chapter, page 168, we mentioned that chemists found it convenient to speak of two kinds of chemical bonds, ionic and covalent. The orbital model for the atom seems to provide an explanation for the formation of ionic bonds. **Ionic bonds** arise when there is *electron exchange between two elements.* **Covalent bonds** are the result of two atoms *sharing electrons.* Does the orbital model prove helpful in understanding covalent bonding?

The answer lies in the electric forces between electrons and protons in atoms. Is the potential energy of the system lowered when a covalent bond forms? The first example is the simplest molecule, H_2.

The orbital model tells us that, for a hydrogen atom in its lowest energy state, the electron is in the 1*s* orbital. In Figure 10-3, a set of drawings shows the energy changes as two hydrogen atoms, *A* and *B*, approach each other. The shading in these drawings shows the electron density averaged over a period of time. At any instant we can imagine the electron at some particular point in the atoms or in the molecule. The protons in these atoms will also be represented with the letters *A* and *B*. The energy of hydrogen atom *A* can be expressed in terms of the average attraction between electron *1* and proton *A*. The electrical attraction depends on the average distance between the electron and proton, r_{1A}. Similarly for hydrogen atom *B*, there is an attractive force between electron *2* and proton *B*. We arbitrarily assign the value of zero for the potential energy of the system when the two atoms are far apart.


A
B
Potential energy
Distance between atoms A and B
r_{AB}
A
B
Potential energy
r_{AB}
A
B
Potential energy
r_{AB}
Potential energy
r_{AB}
Potential energy
r_{AB}

Two hydrogen atoms A and B so far apart that they do not influence each other.

Potential energy decreases as two hydrogen atoms approach each other.

Potential energy reaches its lowest value. Molecule forms.

Potential energy increases as two hydrogen atoms get too close. Nuclear repulsion becomes dominant factor.

Complete potential energy curve for two hydrogen atoms.

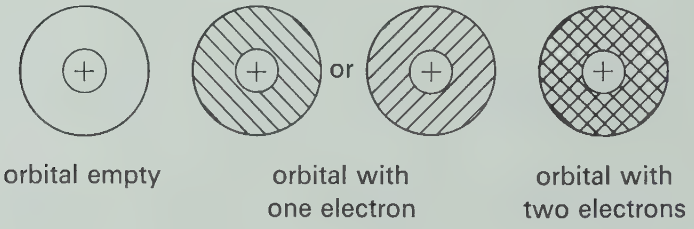
FIGURE 10-3

Potential energy for two hydrogen atoms as they approach and form a covalent bond.

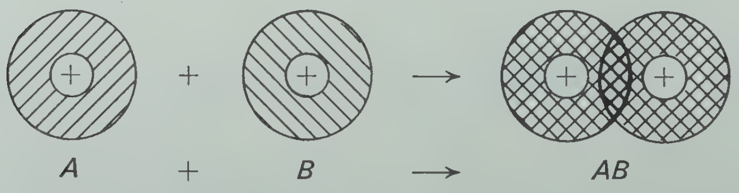
As the two atoms approach each other, electrons *1* and *2* begin to interact with both protons *A* and *B*. The potential energy of the system decreases. Our diagrams show that the orbitals begin to overlap or merge. The probability of finding the electrons between the two protons increases and a chemical bond forms. However, the orbitals cannot merge completely. The repulsive force between the protons *A* and *B* becomes more important than the attractive forces between electrons and protons as the distance between *A* and *B* becomes small.

Figure 10-3 summarizes what happens when two hydrogen atoms approach each other. The system has the lowest potential energy when the two atoms are not too close or not too far apart. The minimum in the potential energy graph occurs at a distance which is the **bond distance** or **bond length** in the hydrogen molecule. There is a balance between the electric forces in the molecule. Electron *1* is now attracted by both protons *A* and *B*. Electron *2* is also attracted by both protons *A* and *B*. There are repulsive forces between the two electrons and between the two protons. For a chemical bond to form between two atoms, the attractive forces must be greater than the repulsive forces.

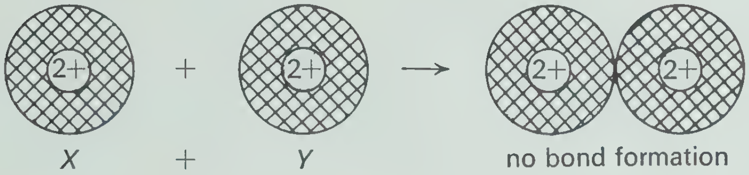
We can simplify our discussion of the chemical bond in the hydrogen molecule using diagrams. We will let a circle represent the orbital. An orbital can be empty, it can have one electron, or it can accommodate two electrons. These possibilities are shown here.



The drawing below shows what happens when two hydrogen atoms approach each other. The circles overlap. The darker cross-hatched area indicates that the two electrons can be near the two protons much of the time. In this overlap region, the electrons are strongly attracted by both protons. Simultaneously, each H atom appears to have acquired two electrons in the 1*s* orbital.



What is the situation for two He atoms? We know from experiments that He_2 is not a stable molecule. Does our orbital model agree with experiment? Helium has two electrons in the 1*s* orbital. As two helium atoms come together, no orbital overlap can take place. The two electrons already in the 1*s* orbital prevent any more electrons entering that space.



Apparently the electrons in one He atom *X* do not get close enough to the nucleus of He atom *Y* to be appreciably attracted toward it. The 1*s* orbitals are already filled up in the helium atoms. No overlap of filled orbitals takes place.

Let's generalize from these two examples. As long as the generalization agrees with experiments, it will be useful.

> Covalent chemical bonds form if valence electrons are shared by two atoms, using partially filled orbitals.

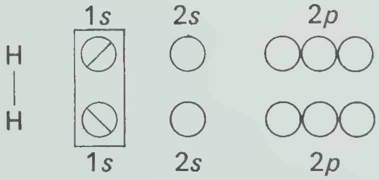
unstable molecule

no bond formation

Covalent bonds will be represented in three ways:
- (a) orbital diagrams.
- (b) a line joining two atoms.
- (c) dots placed between the atoms.

Here are the examples of hydrogen and helium again.

(Bond forms)

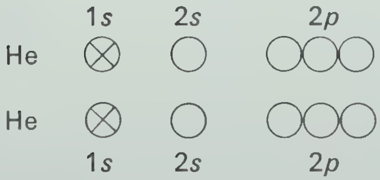


An orbital diagram

or H· + ·H ⟶ H : H

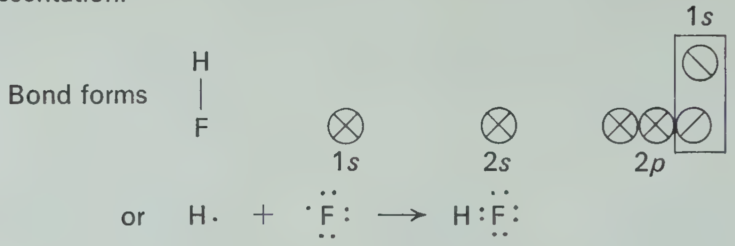
An electron dot diagram

(No bond forms)



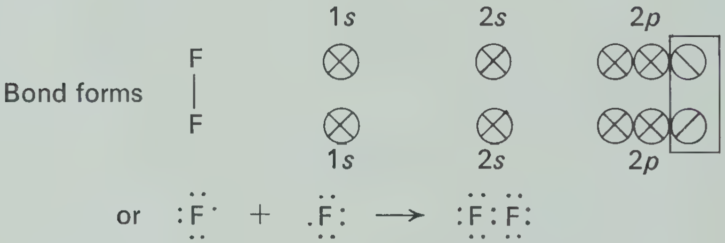
or He : + He : ⟵ He : He :

Do these representations apply to the bond between hydrogen and fluorine? Only valence electrons are shown in the electron dot representation.



The orbital model agrees with the known formula HF for hydrogen fluoride.

It is also easy to show the formation of a fluorine molecule, F_2, with these diagrams.



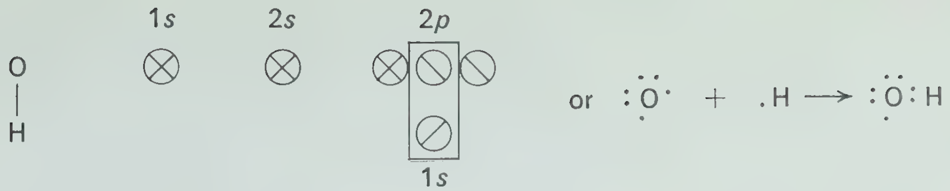
Overlap of the half-filled 2*p* orbitals occurs when two fluorine atoms approach each other. A covalent bond forms.

You may be wondering why the valence electrons for each atom of fluorine in F_2 are indicated by four pairs of dots. Perhaps eight dots equally spaced would be as good. Chemists are suggesting in an electron dot diagram something that is clearly shown in the orbital diagram. Only two electrons can be placed in an orbital. Therefore the four pairs of dots carry the suggestion that the valence electrons are grouped in four orbitals, the 2*s* and the three 2*p* orbitals.

These ideas apply to a large number of molecules. In Section 9-9, electron designations for the elements were derived. At that time we were dealing with the atoms of these elements in the gas phase. Atoms in molecules do not always have the same electron configurations as they do when isolated. The experimentally determined formulas guide us in writing electron configurations for atoms *when they are in molecules.* Table 10-6 contains formulas for the hydrides and fluorides of the first ten elements. These formulas have been determined experimentally by methods similar to the one you used in Experiment 16. We know hydrogen and fluorine usually form one bond per atom. Therefore the number of bonds between H (or F) and another atom suggests the number of unpaired electrons in that other atom. And the number of unpaired electrons suggests an electron configuration for the atom when it is part of a molecule.

We can profit from a closer look at some of these elements. If a hydrogen atom approached an oxygen atom, the formation of a chemical bond can be represented as follows.

Bond forms



The electronic structure for OH is similar to that for the fluorine atom. Each has the electronic structure $1s^2 2s^2 2p^5$. Like the fluorine atom, OH is a very reactive species because it has residual bonding capacity. There is still an unpaired electron. Chemists have been able to detect this molecule in high temperature flames. Recently astronomers have interpreted radiowaves coming from the center of our galaxy to mean that OH molecules may exist in space, between the stars in our galaxy.

There are several ways in which the bonding capacity of the oxygen atom in OH can be satisfied. If another hydrogen atom approached the oxygen atom, the molecule H_2O forms.

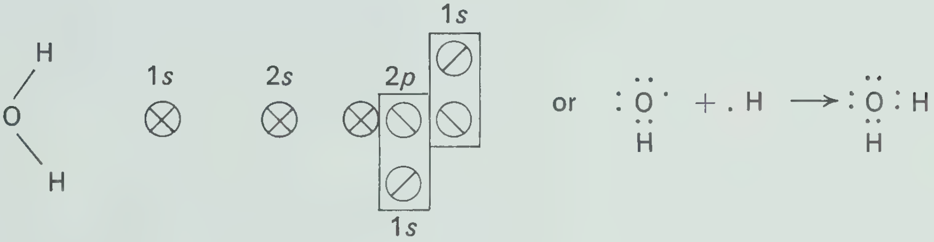


TABLE 10-6

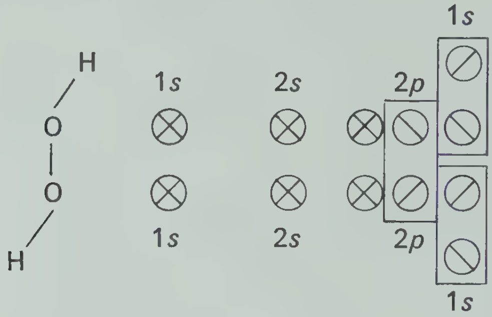
Derived Electron Configurations for the First Ten Elements

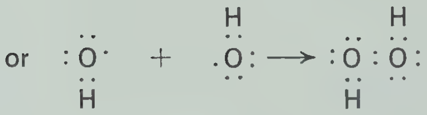
Element	Compound with Hydrogen Formula	Compound with Hydrogen Number of Bonds	Compound with Fluorine Formula	Compound with Fluorine Number of Bonds	Derived Number of Unpaired Electrons per atom of Q	Derived Electron Configuration 1s	2s	2p
H	H_2	1	HF	1	1	⊘	○	○○○
He	—	0	—	0	0	⊗	○	○○○
Li*	LiH	1	LiF		1	⊗	⊘	○○○
Be*	BeH_2	2	BeF_2		2	⊗	⊘	⊘○○
B	(BH_3)**	3	BF_3	3	3	⊗	⊘	⊘⊘○
C	CH_4	4	CF_4	4	4	⊗	⊘	⊘⊘⊘
N	NH_3	3	NF_3	3	3	⊗	⊗	⊘⊘⊘
O	H_2O	2	OF_2	2	2	⊗	⊗	⊗⊘⊘
F	HF	1	F_2	1	1	⊗	⊗	⊗⊗⊘
Ne	—	0	—	0	0	⊗	⊗	⊗⊗⊗

* The lithium and beryllium compounds have ionic structures at room temperature.

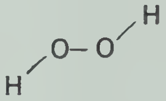
** The molecule BH_3 exists only as a short-lived intermediate in some chemical reactions. The boron hydride, B_2H_6, has the lowest molar mass of the stable compounds of boron and hydrogen. For many years chemists could not account for the bonding in many boron compounds. During the last fifteen years explanations have been found to account for these unusual compounds.

Another possibility is the formation of hydrogen peroxide when two OH molecules approach each other. Compare this diagram with the one for formation of F_2, page 176.

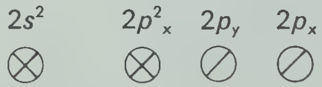



or $\underset{H}{:\overset{..}{\underset{..}{O}}\cdot} + \overset{H}{\cdot\overset{..}{\underset{..}{O}}:} \longrightarrow \underset{H}{:\overset{..}{\underset{..}{O}}}:\overset{H}{\overset{..}{\underset{..}{O}}}:$

The formula for H_2O_2 is somewhat easier to see if the chemical bonds are drawn as lines, not dots. Each line represents a pair of bonding electrons. The valence electrons not involved in bonding are omitted.

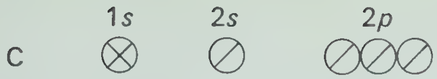


The atoms in H_2O and H_2O_2 are deliberately not drawn in a straight line. Instead a zig-zag arrangement is used. We are trying to suggest the shape or geometry for the molecule when writing the formula in this fashion. Look at the orbital diagram for water again. The valence electrons for oxygen can be written:

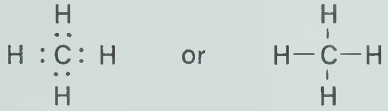


Bond formation with hydrogen atoms can occur if the orbitals on the hydrogen atoms overlap with the $2p_y$ and $2p_z$ orbitals of oxygen. We saw in Figure 9-8 that the $2p$ orbitals do not have spherical symmetry. The electron density is highest along the x or y or z-axes. We expect that the two bonds in H_2O would be perpendicular to each other, one along the y-axis and the other along the z-axis. Although the topic of molecular geometry will not be discussed until Chapter 16, structural formulas are drawn to suggest molecular shapes.

Now look at the carbon atom. Many experiments suggest that the orbital diagram for carbon must contain four unpaired electrons to agree with the formulas CH_4 and CF_4.



Suppose four hydrogen atoms approach a carbon atom. We would expect four bonds to form as the orbitals of the hydrogen atoms overlap with the four orbitals on the carbon atom. Methane, the molecule that forms, can be represented in several ways.

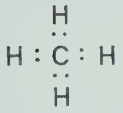


$$\begin{array}{c} \mathrm{H} \\ \cdot\cdot \\ \mathrm{H : C : H} \\ \cdot\cdot \\ \mathrm{H} \end{array} \quad \text{or} \quad \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H} \end{array}$$

EXERCISE 10-2

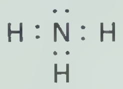
Draw electron dot formulas for the molecules CH_3, CF_3, CHF_3, CH_2F_2, and CH_3F. Which of these would you expect to be extremely reactive?

There are a number of simple molecules which are quite similar in many respects. Let's write out their electron dot formulas.



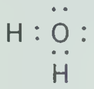
$$\begin{array}{c} \mathrm{H} \\ \cdot\cdot \\ \mathrm{H : C : H} \\ \cdot\cdot \\ \mathrm{H} \end{array}$$

Methane



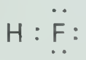
$$\begin{array}{c} \cdot\cdot \\ \mathrm{H : N : H} \\ \cdot\cdot \\ \mathrm{H} \end{array}$$

Ammonia



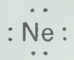
$$\begin{array}{c} \cdot\cdot \\ \mathrm{H : O :} \\ \cdot\cdot \\ \mathrm{H} \end{array}$$

Water



$$\begin{array}{c} \cdot\cdot \\ \mathrm{H : F :} \\ \cdot\cdot \end{array}$$

Hydrogen fluoride



$$\begin{array}{c} \cdot\cdot \\ \mathrm{: Ne :} \\ \cdot\cdot \end{array}$$

Neon

This set of molecules is **isoelectronic** with the noble gas neon. We saw something similar when discussing ionic compounds in Section 10-1. Atoms react to form compounds in which the electronic structures for each atom are the same as one of the noble gases. In methane, ammonia, water, and hydrogen fluoride, each H atom has a pair of electrons in the 1*s* orbital (the He structure). The four atoms C, N, O, and F each has eight electrons in the 2*s* and 2*p* orbitals (the Ne structure).

On page 170, we proposed a generalization that helped us to understand ionic bonding. Let us propose another generalization for covalent bonding.

> Covalent bonding occurs when atoms can share electrons.
>
> Each atom in the compound acquires an electron configuration like that for one of the noble gases.

EXERCISE 10-3

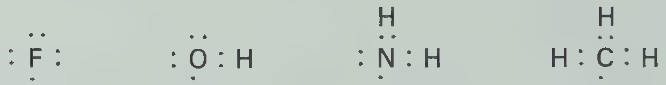
Draw the electron dot formulas for the ions NH_4^+ and H_3O^+. First draw the electron dot formulas for NH_3 and H_2O. Then add H^+ to each formula. H^+ has no electrons.

EXERCISE 10-4

Draw the electron dot formula for ammonium chloride, NH_4Cl.

10-3 Families of Covalent Compounds

In the last section, we pointed out that the molecule OH was similar in electron structure to the fluorine atom, F. The chemical reactivity for these two species is very high. This comparison can be extended to include the very reactive molecules CH_3 and NH_2.



$$:\overset{..}{\underset{.}{F}}: \qquad :\overset{..}{\underset{.}{O}}:H \qquad :\overset{\overset{H}{..}}{\underset{.}{N}}:H \qquad H:\overset{\overset{H}{..}}{\underset{.}{C}}:H$$

When a hydrogen atom approaches each of these, the molecules HF, H_2O, NH_3, and CH_4 form. These molecules have the same electron structure as neon. Also the two molecules, F_2 and H_2O_2, are known to form readily. Table 10-7 lists the molecules that arise when all possible pairs of the reactive molecules combine.

TABLE 10-7

Compounds, Isoelectronic with F_2, Formed from Reactive Molecules

	$\cdot\overset{..}{\underset{..}{F}}:$	$\cdot\overset{..}{\underset{..}{O}}:H$	$\cdot\overset{\overset{H}{..}}{\underset{..}{N}}:H$	$\cdot\overset{\overset{H}{..}}{\underset{\underset{H}{..}}{C}}:H$
$H:\overset{\overset{H}{..}}{\underset{\underset{H}{..}}{C}}\cdot$	$H_3C—F$	$H_3C—OH$	$H_3C—NH_2$	$H_3C—CH_3$
$H:\overset{\overset{H}{..}}{\underset{..}{N}}\cdot$	$H_2N—F$	$H_2N—OH$	$H_2N—NH_2$	
$H:\overset{..}{\underset{..}{O}}\cdot$	$HO—F$	$HO—OH$		
$:\overset{..}{\underset{..}{F}}\cdot$	$F—F$			

EXERCISE 10-5

Convince yourself that the electron dot formulas for CH_3OH (methyl alcohol) and $NH_2—NH_2$ (hydrazine) are the same as the electron dot formula for F_2 (fluorine).

The results in Table 10-7 are important. First, our generalization on covalent bonding has guided us to the correct electron structure of ten more molecules. Second, we can predict some of the chemical and physical properties of these substances. Look at H_2O_2, CH_3OH, and C_2H_6. It seems reasonable to expect hydrogen peroxide, H_2O_2, to have some properties rather similar to water. And ethane, C_2H_6, should have properties like methane, CH_4, but not at all like water. The substance, methyl alcohol, CH_3OH, should have properties like water in some respects and like methane in others. After all, half of the molecule CH_3OH resembles methane, $CH_3—H$, and the other half resembles water, $H—OH$.

10-4 Hydrocarbons

In the last section, we discussed how "double" molecules arise. Of all the elements, carbon shows the greatest tendency to form molecules with several atoms of the same kind joined in a chain. Let us start with methane to illustrate what we mean. Although our examples do not correspond with the usual methods of synthesizing these compounds, the structure of each molecule is correct.

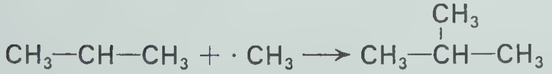
1.
$$CH_4 \longrightarrow \cdot CH_3 + H \cdot$$
$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3—CH_3 \qquad \text{ethane}$$

2.
$$CH_3—CH_3 \longrightarrow CH_3—CH_2 \cdot + \cdot H$$
$$CH_3—CH_2 \cdot + \cdot CH_3 \longrightarrow CH_3—CH_2—CH_3 \qquad \text{propane}$$

3.
$$CH_3—CH_2—CH_3 \longrightarrow CH_3—CH_2—CH_2 \cdot + \cdot H$$
$$CH_3—CH_2—CH_2 \cdot + \cdot CH_3 \longrightarrow CH_3—CH_2—CH_2—CH_3 \qquad \text{normal butane}$$

There is another way for propane to "grow".

4.
$$CH_3—CH_2—CH_3 \longrightarrow CH_3—CH—CH_3 + \cdot H$$



$$CH_3—CH—CH_3 + \cdot CH_3 \longrightarrow CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}H—CH_3$$

iso-butane

The two butanes are given different names — normal or *n*-butane and *iso* or *i*-butane. They have the same molecular formula (C_4H_{10}) but different **structural formulas.** Normal butane has four carbon atoms linked in a linear fashion; isobutane has four carbon atoms linked in a branched fashion. Substances that have the same molecular formula but different structural formulas are called **isomers.**

The molecules named above are examples of carbon-hydrogen compounds called **saturated hydrocarbons** or **alkanes.** They are the principal components of natural gas and are an important energy source. An extensive network of pipelines in the United States brings natural gas to many cities. Many of our homes are heated with natural gas. Some of the properties of these substances are given in Table 10-8.

TABLE 10-8

Properties of Some Hydrocarbons

Name	Molecular Formula	Molar Mass, grams	Melting Temperature, °C	Boiling Temperature, °C
Methane	CH_4	16	−182.5	−161.5
Ethane	C_2H_6	30	−183.3	−88.6
Propane	C_3H_8	44	−187.7	−44.1
n-butane	$n\text{-}C_4H_{10}$	58	−138.4	−0.5
iso-butane	$i\text{-}C_4H_{10}$	58	−159.6	−11.7

There is a way to express the molecular formula for any hydrocarbon in this family. Perhaps you have noticed in our four examples that each new member adds the unit $—CH_2—$ to the preceding member. The general formula can be written:

$$C_nH_{2n+2}$$

Any hydrocarbon fitting this general formula is a member of this family, the **saturated hydrocarbons.**

EXERCISE 10-6

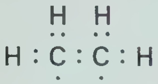
The next compound in the saturated hydrocarbon family would have five carbon atoms. The name *pentane* is used for this compound. Show how pentane can "grow" from each of the butane isomers. How many isomers of pentane would you expect? Draw them.

10-5 Molecules with Double Bonds

In the last two sections we have discussed a number of molecules which have single bonds. This statement means one orbital of atom *A* overlaps with one orbital of atom *B*. We have represented that situation with electron dot structures or with line structures. For example, the bonding in hydrogen fluoride can be described in several ways. Here are two.

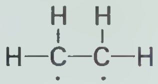
$$\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}: \qquad \text{or} \qquad \mathrm{H}—\mathrm{F}$$

There are many molecules that are best described in terms of **double bonds.** The orbital model provides an explanation for these molecules. The hydrocarbon ethylene is used to illustrate double bonds. Ethylene, C_2H_4, has two fewer hydrogen atoms than ethane, C_2H_6. Suppose we try to write an electron dot formula for ethylene, using only single bonds. The result is



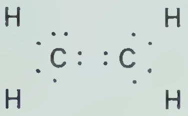
$$\mathrm{H} : \overset{\mathrm{H}}{\underset{\cdot}{\ddot{\mathrm{C}}}} : \overset{\mathrm{H}}{\underset{\cdot}{\ddot{\mathrm{C}}}} : \mathrm{H}$$

or

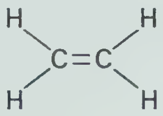


$$\mathrm{H}-\overset{\mathrm{H}}{\underset{\cdot}{\overset{|}{\mathrm{C}}}}-\overset{\mathrm{H}}{\underset{\cdot}{\overset{|}{\mathrm{C}}}}-\mathrm{H}$$

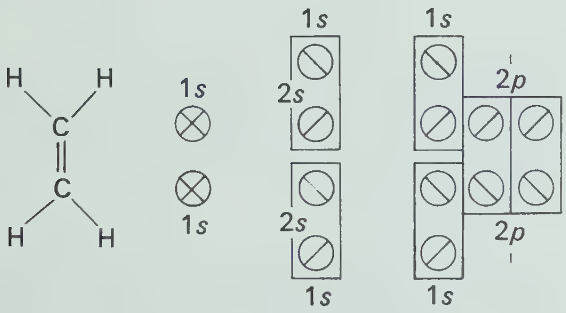
These formulas show two unpaired electrons. From earlier examples, OH and CH_3, this unused bonding capacity would suggest very high reactivity for ethylene. But ethylene does not have the activity of a compound with unpaired electrons. There is a way to use up the bonding capacity in ethylene within the molecule. The two electrons can be paired.



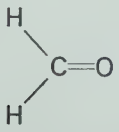
or



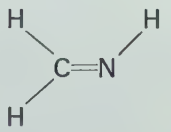
The carbon atoms are said to be joined by a **double bond.** Eight valence electrons are placed around each carbon atom (the neon structure) and two electrons are placed near each hydrogen atom (the helium structure). The only new idea that appears in the ethylene structure is the placement of four electrons between the two carbon atoms.



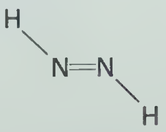
Double bonds appear in molecules when two orbitals of atom *A* overlap with two orbitals of atom *B*. These molecules are isoelectronic with ethylene.



formaldehyde

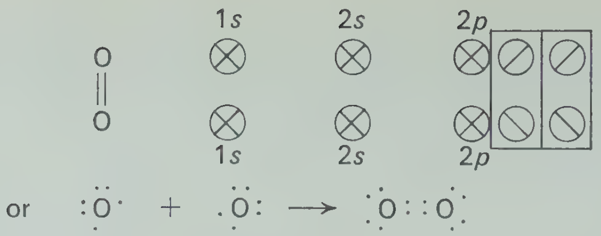


ethylene imine



di-imine

Oxygen, O_2, is isoelectronic with ethylene and it would seem straightforward to predict that O_2 would have a double bond.



The structure of oxygen has proved to be a challenge to chemists. Many of the properties of oxygen are consistent with this structure of O_2. The bond in the oxygen molecule is stronger than the single bond between oxygen atoms in hydrogen peroxide (page 178). More energy is required to break the bond in O_2 than is required for the bond in H_2O_2. In addition, the bond length in the O_2 molecule is shorter than the oxygen-oxygen bond in H_2O_2. The short bond length in the O_2 molecule shows that the two oxygen atoms are drawn together more effectively than in H_2O_2. These experimental facts suggest that there are extra bonding electrons between the two oxygen atoms in O_2.

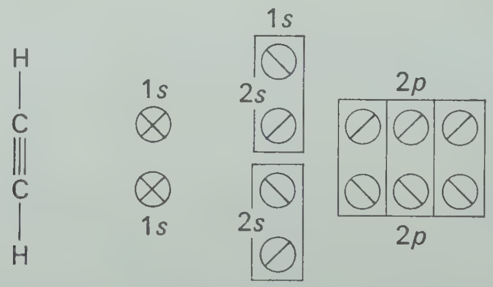
However, other experimental measurements are not in agreement with the double bond description for O_2. These measurements indicate that there are two unpaired electrons in O_2. Our simple model for chemical bonding is only partially correct for one of the most important molecules. However, this model does give satisfactory explanations for a very large number of compounds. We will not discuss the more complex model which gives adequate treatment of O_2.

10-6 Molecules with Triple Bonds

The hydrocarbon acetylene is a good example of a molecule with a triple bond. Acetylene has the molecular formula C_2H_2. The neon and helium configurations are achieved when we assign these structures for acetylene.

H : C : : : C : H or H—C≡C—H

The orbital representation for this molecule looks like this.



Nitrogen and hydrogen cyanide are isoelectronic with acetylene.

N≡N H—C≡N· H—C≡C—H

Our discussion of covalent bonding has been limited to compounds of the second row elements, C, N, O, and F. From our earlier discussion of the Periodic Table, we would expect to find that our explanations of covalent bonding would be applicable to all elements in the same periodic family. The same orbital representations would explain the bonding in Cl_2, Br_2, and I_2; in H_2S, H_2Se, and H_2Te; in CCl_4, CBr_4, and CI_4. Of course, the overlapping orbitals would have higher quantum numbers than the orbitals used in the compounds F_2, H_2O, and CF_4.

Figures 10-4 and 10-5 show the increase in melting and boiling temperatures for the noble gases, the halogens, and the carbon compounds with general formula CX_4.

Figures 10-6 and 10-7 show plots of melting and boiling behavior for hydrides of elements in the columns under C, N, O, and F. Periodic trends are evident *if we ignore the first compound in each series.* Water, ammonia, and hydrogen fluoride seem to have abnormally high melting and boiling temperatures. Does our orbital model suggest any explanation for these experimental facts?

High melting and boiling temperatures suggest greater forces between molecules of HF, H_2O, and NH_3 than we might expect. Perhaps we are dealing with aggregates or clusters of molecules with lowered potential energy. Clustering of ions led to lowering of potential energy for the ionic system (page 169), and something similar may provide an explanation for the higher melting and boiling temperatures. Perhaps hydrogen atoms serve as a bridge to join

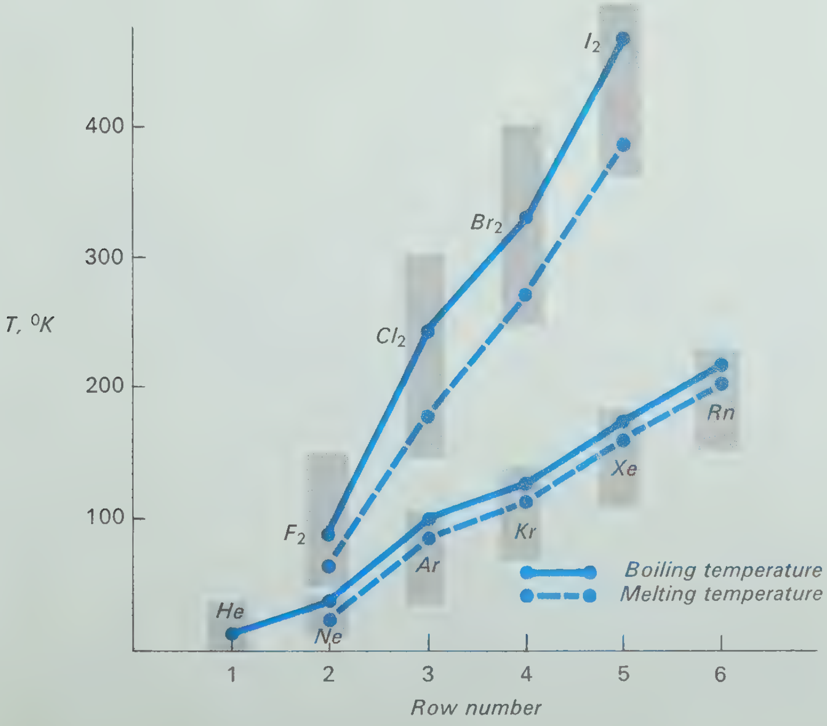


FIGURE 10-4

The melting and boiling temperatures of the noble gases and of the halogens.

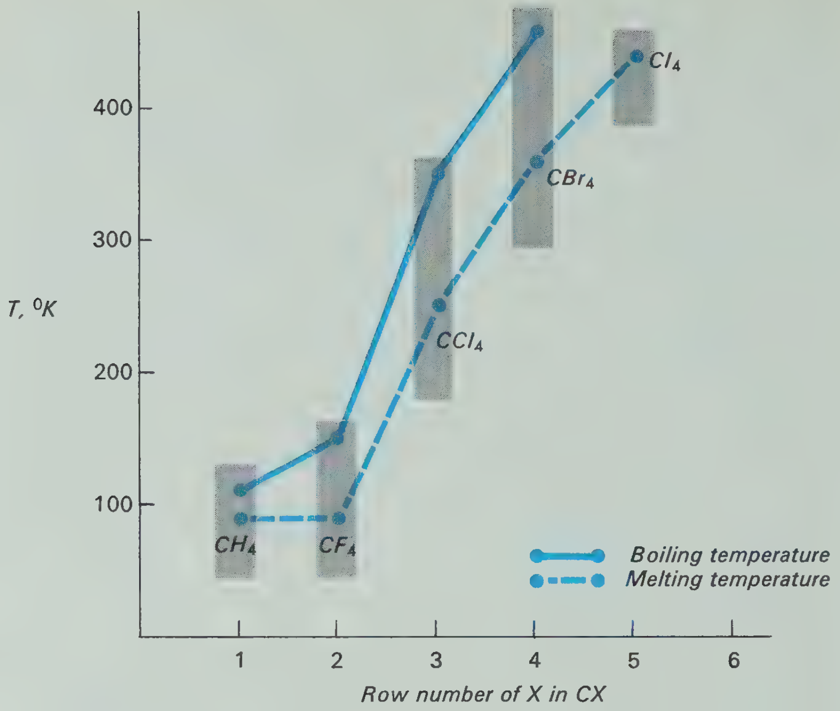


FIGURE 10-5

The melting and boiling temperatures for carbon compounds with formula CX_4.

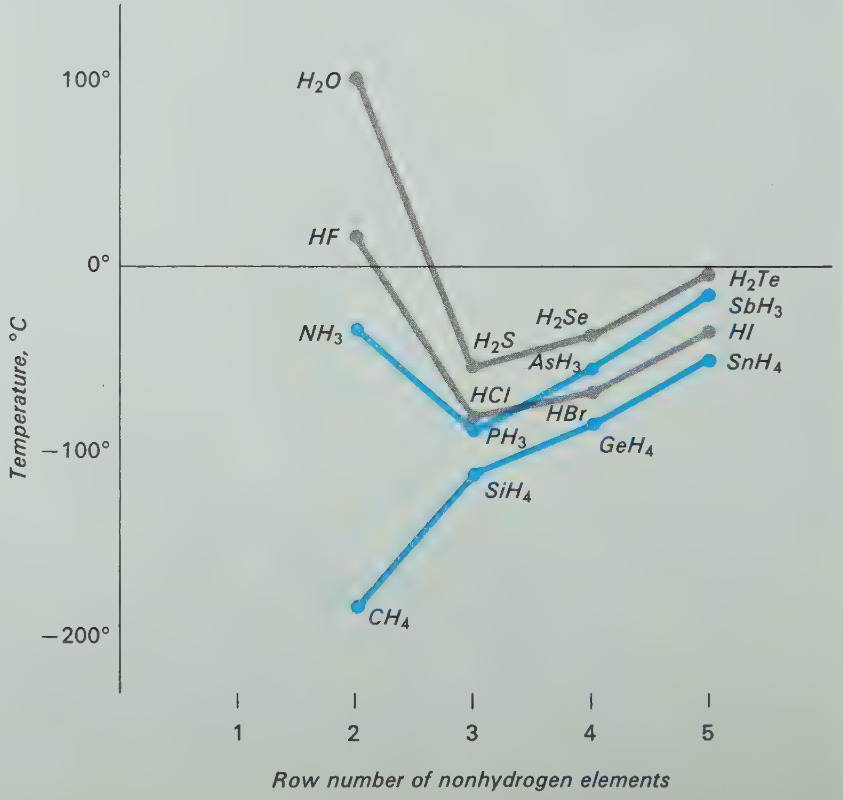


FIGURE 10-6

Trends in boiling temperatures for hydrides of four families.

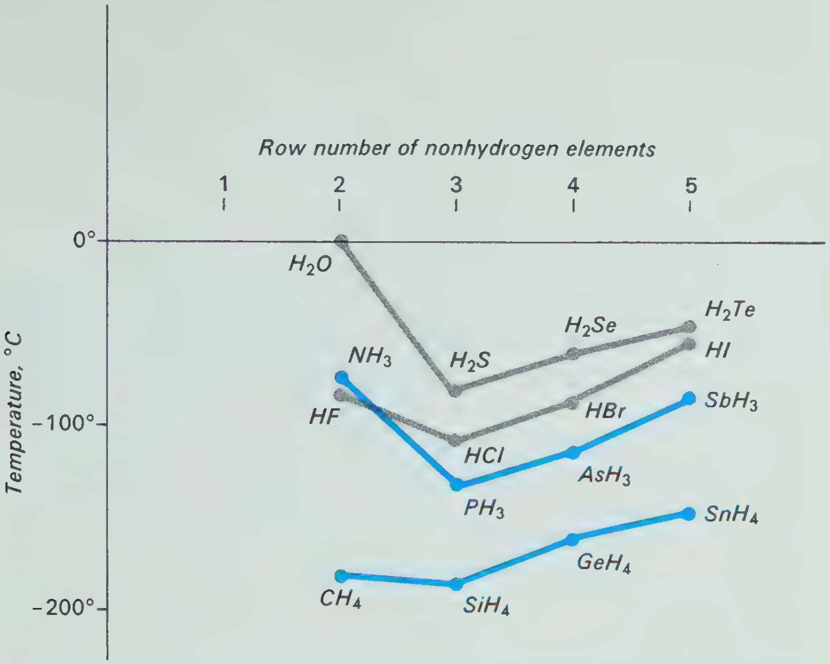
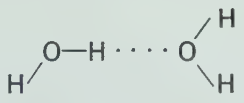


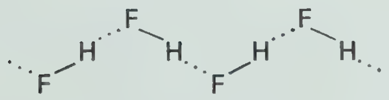
FIGURE 10-7

Trends in the melting temperatures for hydrides of four families.

several molecules together. This bridge would provide the clusters that we need. This type of bonding is given the name **hydrogen bonding.** It is often represented in this manner:



or

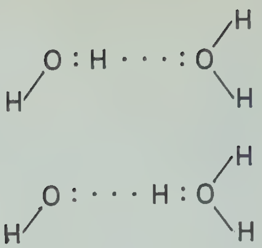


We are not ready to provide an explanation for hydrogen bonding. However, we can offer a qualitative view that will be discussed more completely in Chapter 17. The clue lies in the fact that the hydrogen atom, with only the 1*s* orbital for bond formation, cannot form two covalent bonds. And yet our suggestion above implies that hydrogen is involved in more than one bond.

At various times we have emphasized that all chemical bonds arise for the same reason. An electron is simultaneously attracted to two nuclei. The same situation holds in hydrogen bonding, with a slight change.

> Hydrogen bonding occurs when the hydrogen nucleus is simultaneously attracted to two electron pairs.

Consider two oxygen atoms in two adjacent water molecules, as in these diagrams.



Two requirements must be met for hydrogen bonding to occur between two molecules. One molecule must contain hydrogen. One molecule must have easily accessible electrons. Often these electrons are supplied by a small atom which has electrons not already involved in bonding. The second requirement explains why hydrogen bonding is most common for compounds containing the atoms F, O, and N (and to a lesser extent Cl). Sometimes hydrogen bonding occurs within one molecule; more often hydrogen bonding occurs between two molecules which do not have to be identical.

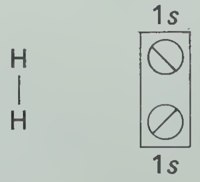
Hydrogen bonding is important in a number of chemical systems. It is particularly important in many biological systems. We will refer to hydrogen bonding in the succeeding chapters of this book.

10-8 Review

In this chapter, we have used the words **ionic bond** and **covalent bond** in discussing chemical bonding. In either case, the nature of the chemical bond is the same: *electrons in atoms are simultaneously attracted by two nuclei.*

The orbital model for the atom helps us in understanding chemical bonds. In ionic bonding, electrons are **transferred** from one element to another element. Positive and negative ions form, each ion having acquired the electron configuration of a noble gas. The electrical attraction between these ions leads to the formation of an ionic solid. Positive ions alternate with negative ions in such a manner that electrical neutrality is achieved.

In covalent bonding, electrons are **shared** by two elements. Sharing can occur when each element has a partially filled orbital. A number of different diagrams are used by chemists in trying to indicate the formation of a covalent chemical bond. The orbital representation of covalent bonding shows most clearly what happens.



Bond forms; the 1*s* orbitals of two H atoms overlap.

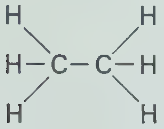
Much simpler but less detailed is the electron dot method of showing the formation of a covalent bond.

$$H\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}: \longrightarrow H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$$

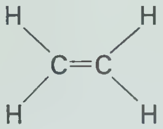
We say that the H atom has acquired the He electron configuration in this molecule. At the same time the F atom has acquired the Ne electron configuration. Still simpler but very convenient is the use of a line to represent the bonding electron pair.

$$H—F$$

A **single bond** arises when an orbital of one atom overlaps an orbital of a second atom. If two orbitals of an atom overlap two orbitals of a second atom, we say that a **double bond** exists between the atoms. The bonding in the three hydrocarbons ethane, ethylene, and acetylene illustrates single, double, and triple bonds.



ethane



ethylene

$$H—C\equiv C—H$$

acetylene

The chapter concludes with a brief discussion of **hydrogen bonding.** Under certain circumstances the H atom acts as a bridge between molecules, giving rise to a cluster of molecules. One consequence of this phenomenon is the unusually high melting and boiling temperatures for water. Hydrogen bonding is particularly important in many biological systems.

Questions and Problems for Chapter 10

1

Which of the properties listed are characteristic of an ionic solid?

(a) low melting temperature.
(b) conducts electricity as a solid.
(c) dissolves in water to form a solution containing mostly ions.
(d) dissolves to form a solution containing mostly molecules.
(e) when fused, the melt conducts electricity.

2

Which families of elements tend to form ionic solids?

3

Describe the electron configuration for atoms of lithium and fluorine after they have reacted to form an ionic solid.

4

How many atoms of fluorine are needed per atom of calcium to form the ionic compound calcium fluoride?

5

Write the empirical formulas, assuming that these elements react to form ionic compounds. The atomic number is given to help you locate the element in the Periodic Table

(a) Al(13) and S(16)
(b) Mg(12) and N(7)
(c) Ba(56) and At(85)
(d) Fr(87) and 0(8)
(e) Ra(88) and I(53)

6

Add the energy term E to the equations

(a) $K \longrightarrow K^+ + e^-$
(b) $K^+ + I^- \longrightarrow KI$

7

Draw the orbital representations of

(a) sodium fluoride, NaF
(b) beryllium fluoride, BeF_2.

8

Give the orbital and also the electron dot representations for H, H^+, and H^-.

9

What type of bonding would you expect to find in MgO? Explain.

10

Show that NaF and MgO are isoelectronic compounds. How would you expect their melting temperatures to compare?

11

In general, what conditions cause two atoms to combine to form:

(a) a bond that is mainly covalent;
(b) a bond that is mainly ionic.

12

What are the molecular species present in gaseous neon, argon, krypton, and xenon? Explain.

13

What energy condition must exist if a chemical bond is to form between two approaching atoms?

14

What valence orbital and valence electron conditions must exist if a chemical bond is to form between two approaching atoms?

15

Give the orbital and also the electron dot representations for the bonding in these molecules: Cl_2, HCl, Cl_2O.

16

Using the electron dot representation, show a neutral, a negatively charged, and a positively charged OH group.

17

Draw the orbital representation of the molecule N_2H_4, hydrazine.

18

Draw electron dot formulas of compounds that are isoelectronic with Cl_2. Use the Periodic Table and the examples in Tables 10-7 as guides.

19

Knowing the orbitals carbon uses for bonding, use the Periodic Table to predict the formula of the chloride of silicon. What orbitals does silicon use for bonding?

20

The borohydride ion, BH_4^-, can be thought of as a combination of BH_3 and H^- ion. Give the orbital and also the electron dot representation for the borohydride ion.

21

Make use of your answer to Problem 20 to describe the bonding in the compounds sodium borohydride and lithium aluminum hydride.

22

Draw electron dot formulas for the molecules CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4.

23

In Section 10-4, we showed how the hydrocarbon family C_nH_{2n+2} can be derived from methane. Similar families of compounds can be derived from methyl alcohol.

(a) Show how ethyl and propyl alcohols, C_2H_5OH and C_3H_7OH, can be derived from methyl alcohol, CH_3OH.
(b) How many isomers would you expect for propyl alcohol?

24

Ethylene is the first of a family of hydrocarbons called *alkenes*. Each alkene has one double bond in the structure. Use line drawings to show bonding in the compounds ethylene and propylene, C_3H_6.

25

Acetylene is the first of a family of hydrocarbons called *alkynes*. Each alkyne has one triple bond in the structure. Use line drawings to show bonding in the compounds acetylene and propyne, C_3H_4.

Energy Effects in Chemical Reactions

11

Now that we have some understanding of molecular structure, let us see what happens when molecules react with one another. We shall discover that chemical reactions form the heart of chemistry. In the next five chapters chemical reactions are considered from several viewpoints. Of course, as before, we will be searching for regularities to help simplify and organize our observations.

When a chemical reaction occurs, some bonds in molecules are broken and new bonds form. Energy is required to break a chemical bond. However, energy is released when new chemical bonds form. Almost all of the energy effects in a chemical reaction are the result of bond-breaking and bond-forming events.

For many years man has depended on chemical fuels to satisfy most of his energy requirements. At first wood was the important fuel. During the last one hundred and fifty years we have used coal, petroleum, and, more recently, natural gas to supply the major energy requirements for our rapidly expanding technology. The rate at which these resources are consumed, however, increases each year. Since there is a limited reserve of chemical fuels, many scientists and engineers are exploring ways to develop nuclear energy as an economical energy source.

Why do some reactions release energy? How is energy stored in molecules? What is the source of this energy? How can it be measured? And how can this energy be released when needed? We will look at some chemical reactions in search of answers to these questions.

11-1 Heat Energy and Chemical Reactions

When soft coal is heated out of contact with air, a number of very important chemical compounds can be separated by distillation. The material left behind is almost pure carbon. It is called coke, a hard, brittle substance that burns with an intense heat, without smoke. It is an important industrial fuel, widely used in blast furnaces in the production of iron. Coke is also used to make a gaseous fuel called "water gas."

At temperatures near 600°C, steam passed over hot coke reacts to give carbon monoxide and hydrogen.

$$H_2O(g) + C(s) \longrightarrow CO(g) + H_2(g)$$

The mixture of product gases is called "water gas." It is an excellent industrial fuel. In the preparation of water gas, a chemical engineer finds by experiment that heat energy is absorbed during the reaction. Periodically the steam must be turned off and the coke reheated to keep the reaction going. It is possible to measure the amount of heat energy absorbed by the system and write it as part of the chemical reaction. Such a measurement shows that 31.4 kcal of heat energy is absorbed for every mole of carbon that reacts. Since heat energy needs to be supplied, it is placed on the left side of the equation.

$$H_2O(g) + C(s) + 31.4\ \text{kcal} \longrightarrow CO(g) + H_2(g)$$

Suppose a mechanical engineer wants to design a boiler which is to be heated by burning water gas as the fuel. There are two chemical reactions that occur when water gas is burned in air:

$$CO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g)$$

and

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(g)$$

These reactions release heat energy. The mechanical engineer would like to know how much. He can find out by measuring the heat energy produced for each reaction. It is placed on the right side of the chemical equation. Experiments give these values:

$$CO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g) + 67.6\ \text{kcal}$$
$$H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(g) + 57.8\ \text{kcal}$$

The total heat energy released is 125.4 kcal when one mole of $CO(g)$ and $H_2(g)$ is burned.

Suppose an accountant decides to look into the cost of using water gas as a fuel. He thinks in terms of gains and losses. He observes that the consumption of coke and water to generate water gas is followed by the burning of water gas to form carbon dioxide and water. He can see that the overall reaction is combustion of coke to form carbon dioxide.

$$\begin{array}{rcl}
H_2O(g) + \quad C(s) & \longrightarrow & CO(g) + H_2(g) \\
CO(g) + \tfrac{1}{2}\,O_2(g) & \longrightarrow & CO_2(g) \\
H_2(g) + \tfrac{1}{2}\,O_2(g) & \longrightarrow & H_2O(g) \\
\hline
C(s) + \quad O_2(g) & \longrightarrow & CO_2(g) \qquad \text{overall reaction}
\end{array}$$

The accountant might ask, "Why not burn the coke directly and save the cost of manufacturing the water gas?"

The mechanical engineer wants to know, "How much heat energy will the boiler receive if I use coke instead of water gas?"

The chemical engineer must go to the laboratory for answers to these questions. He measures the heat energy released when one mole of carbon is burned. The experiment shows that 94.0 kcal/mole is released.

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 94.0\ \text{kcal}$$

The chemical engineer now can answer the accountant's questions. If one mole of carbon is burned directly, 94.0 kcal of heat energy is released. If one mole of carbon is converted to water gas and then burned, 125.4 kcal can be obtained. The mechanical engineer has a better fuel.

The accountant might ask the chemical engineer, "Where did this extra heat energy come from? Did we get something for nothing?" The answer to this last question is "No." Water gas releases more heat energy per mole of carbon because energy was stored in the system when hot coke reacted with steam. The accountant can balance his books this way.

TABLE 11-1

Heat Effects in the Manufacture and Use of Water Gas

Reactions	Heat Energy Input	Heat Energy Outflow
$H_2O(g) + C(s) \longrightarrow CO(g) + H_2(g)$	31.4 kcal	
$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$		67.6 kcal
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$		57.8 kcal
	31.4 kcal absorbed	125.4 kcal released
Net reaction $C(s) + O_2(g) \longrightarrow CO_2(g)$		125.4 kcal −31.4 kcal
	Net energy released	94.0 kcal

Our example shows that 31.4 more kcal were stored in the water gas than in the starting materials, coke and steam. We can get that energy back any time we want it, by burning the water gas. The energy is stored as potential energy in the H_2 and CO molecules. The bonds in these molecules have more stored energy than those in C and H_2O.

11-2 Heat Content of a Substance

When sunlight falls on the leaves of a tree, chlorophyll molecules receive some of the radiant energy. An amazing chemical factory is set into operation. Molecules of water and carbon dioxide are converted into sugar molecules and oxygen molecules.

$$6\ H_2O + 6\ CO_2 + \text{energy} \longrightarrow C_6H_{12}O_6 + 6\ O_2$$

In photosynthesis the energy in sunlight is transformed into potential energy represented by a new arrangement of atoms. The energy is stored in sugar molecules and in oxygen molecules. Chemists have a special name for this type of potential energy. The potential energy stored in a substance during its formation is called the **heat content** of the substance. A mole of each substance has a characteristic heat content just as it has a characteristic mass. Chemists use the symbol H to represent **molar heat content.** The heat effect in a chemical reaction is the difference between the heat contents of the products and the heat contents of the reactants. This difference is represented by the symbol ΔH. The Greek letter Δ, delta, is shorthand for difference.

$$\text{Heat of reaction} = \Delta H = \begin{pmatrix}\text{Heat content}\\ \text{of products}\end{pmatrix} - \begin{pmatrix}\text{Heat content}\\ \text{of reactants}\end{pmatrix}$$

Remember, *almost all of the energy effects in a chemical reaction are the result of bond-breaking plus bond-forming events.*

To help you remember how ΔH is defined, think a minute how you would calculate the time it takes you to get to school each day. Suppose you leave home at 7:15 each morning and arrive at school at 7:50. The time required for this trip would, of course, be 35 minutes.

$$\begin{aligned}\text{Change in time} &= \text{Final time} - \text{Initial time}\\ &= 7{:}50 - 7{:}15\\ \Delta(\text{time}) &= 35 \text{ minutes}\end{aligned}$$

Chemists agreed many years ago to calculate quantities like ΔH in this manner:

$$(\text{value at final conditions}) - (\text{value at initial conditions})$$

The water gas example will help us to understand ΔH better. Here are equations for the two reactions.

$$H_2O(g) + C(s) + 31.4\ \text{kcal} \longrightarrow H_2(g) + CO(g)$$

$$CO(g) + \tfrac{1}{2}\ O_2(g) \longrightarrow CO_2(g) + 67.6\ \text{kcal}$$

The first reaction absorbs heat energy. It is an *endothermic* reaction. The second reaction gives off heat energy. It is an *exothermic* reaction. If you can imagine yourself standing inside the reaction chamber for each of these reactions, you would be able to say:

"Heat energy is being added to the first system. The heat content of the products must be greater than the heat content of the reactants."

"Heat energy is being given off by the second system. The heat content of the products must be less than the heat content of the reactants."

We can rewrite the chemical equations to agree with this description. This method shows a ΔH term after each equation. Note that the sign of ΔH makes sense if you consider yourself part of the system.

ENDOTHERMIC REACTION

The sign of ΔH is positive if energy must be added to the system.

$$H_2O(g) + C(s) + 31.4\text{ kcal} \longrightarrow CO(g) + H_2(g)$$
$$\Delta H = +31.4\text{ kcal}$$

ΔH is positive for an endothermic reaction. The heat content of the system increases.

EXOTHERMIC REACTION

The sign of ΔH is negative if the system gives out energy.

$$CO(g) + {}^1\!/_2\, O_2(g) \longrightarrow CO_2(g) + 67.6\text{ kcal}$$
$$\Delta H = -67.6\text{ kcal}$$

ΔH is negative for an exothermic reaction. The heat content of the system decreases.

These ideas are presented graphically in Figures 11-1 and 11-2.

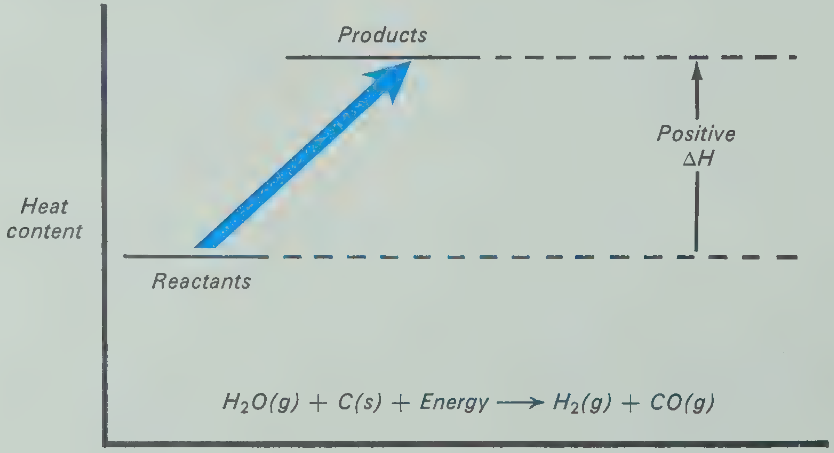

Products
Positive
ΔH
Heat content
Reactants
$H_2O(g) + C(s) + Energy \longrightarrow H_2(g) + CO(g)$

FIGURE 11-1

Change in heat content during an endothermic reaction. The system gains energy.

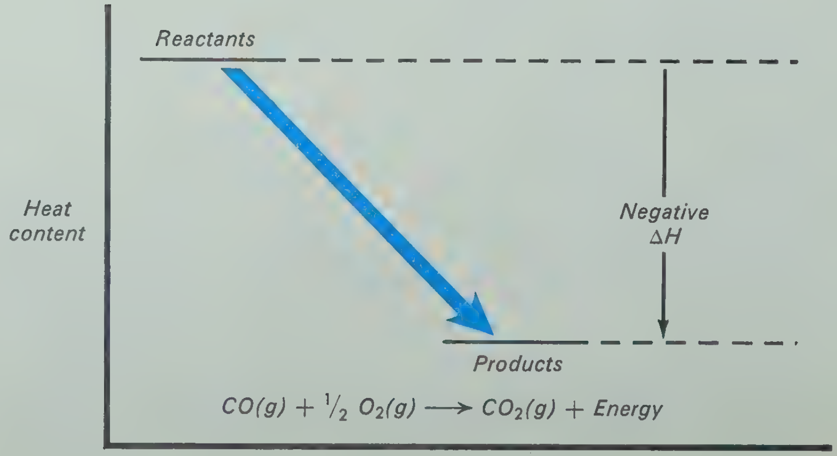

Reactants
Heat content
Negative
ΔH
Products
$CO(g) + {}^1\!/_2\, O_2(g) \longrightarrow CO_2(g) + Energy$

FIGURE 11-2

Change of heat content during an exothermic reaction. The system loses energy.

11-3 Measurement of Heats of Reaction

You have measured heat effects for a number of chemical reactions in your own laboratory work. You found, for example, that the reaction between aluminum metal and a solution of copper chloride generated a large amount of heat. In the more careful work of Experiment 26, you determined the heat of reaction when one mole of an acid reacted with one mole of base.

The heat of a chemical reaction is measured with a **calorimeter**. Several kinds of calorimeters are illustrated in Figure 11-3. You used the kind on the left. A more elaborate calorimeter is shown in schematic form in the center of the figure. The chemical reaction between known masses of substances is allowed to take place in the reaction chamber, *A*. The heat effect of this reaction changes the temperature of the water in the insulated reservoir, *B*. If we know the mass of water and the temperature change, we can calculate the heat energy, in calories, for the chemical reaction. This is the same method you employed in Experiment 26, using a plastic cup as the calorimeter. It is customary to report the molar heat of reaction. Chemists have measured the heats of many reactions. Often they use a very complex calorimeter to achieve precise results. The right-hand section of Figure 11-3 illustrates one. A few examples of molar heats of reaction are given in Table 11-2.

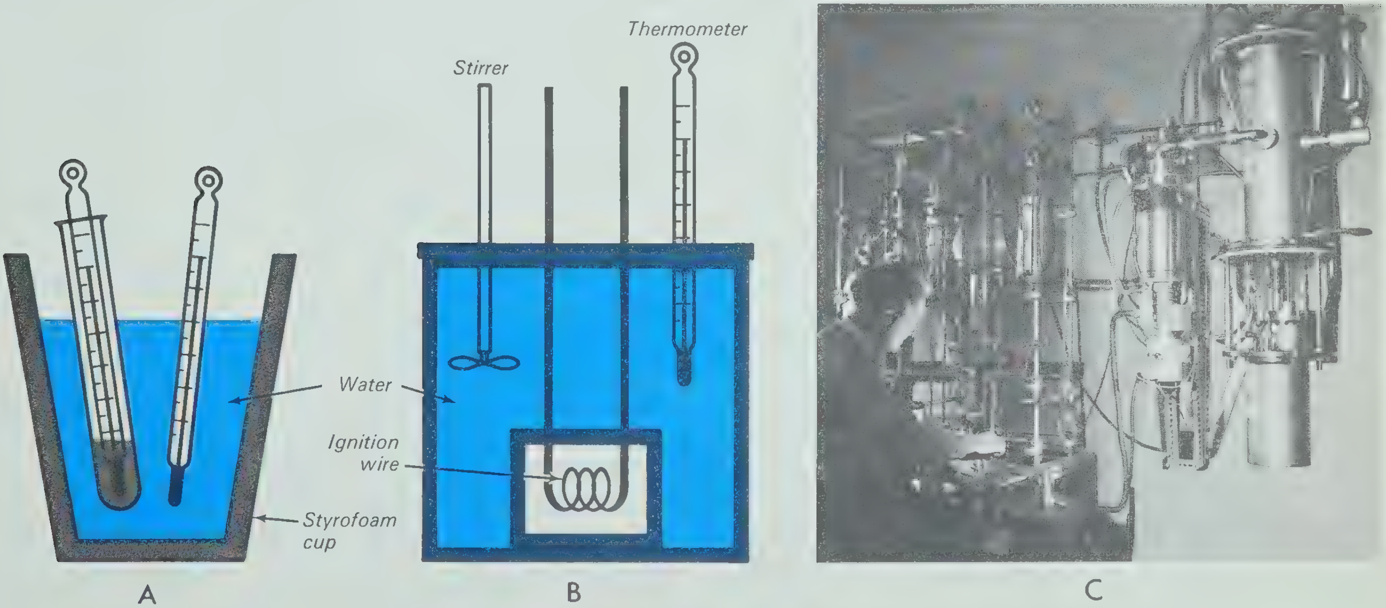


FIGURE 11-3

A. A simple calorimeter to measure heats of reaction in aqueous solutions.
B. Schematic drawing of a calorimeter.
C. Complex calorimeter.

TABLE 11-2

Heats of Reaction Between Elements

$t = 25°C$ $\quad$ $p = 1$ atmosphere

Elements		Compound Formula	Compound Name	Heat of Reaction (kcal/mole of product)
$H_2(g) + \frac{1}{2}O_2(g)$	$\longrightarrow$	$H_2O(g)$	water vapor	−57.8
$H_2(g) + \frac{1}{2}O_2(g)$	$\longrightarrow$	$H_2O(l)$	liquid water	−68.3
$\frac{1}{8}S_8(s) + O_2(g)$	$\longrightarrow$	$SO_2(g)$	sulfur dioxide	−71.0
$H_2(g) + \frac{1}{8}S_8(s) + 2\,O_2(g)$	$\longrightarrow$	$H_2SO_4(l)$	sulfuric acid	−194
$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$	$\longrightarrow$	$NO(g)$	nitric oxide	+21.6
$\frac{1}{2}N_2(g) + O_2(g)$	$\longrightarrow$	$NO_2(g)$	nitrogen dioxide	+ 8.1
$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$	$\longrightarrow$	$NH_3(g)$	ammonia	−11.0
$C(s) + \frac{1}{2}O_2(g)$	$\longrightarrow$	$CO(g)$	carbon monoxide	−26.4
$C(s) + O_2(g)$	$\longrightarrow$	$CO_2(g)$	carbon dioxide	−94.0
$C(s) + 2\,H_2(g)$	$\longrightarrow$	$CH_4(g)$	methane	−17.9
$2\,C(s) + 3\,H_2(g)$	$\longrightarrow$	$C_2H_6(g)$	ethane	−20.2
$3\,C(s) + 4\,H_2(g)$	$\longrightarrow$	$C_3H_8(g)$	propane	−24.8
$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s)$	$\longrightarrow$	$HI(g)$	hydrogen iodide	+ 6.2
$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$	$\longrightarrow$	$HI(g)$	hydrogen iodide	− 1.2

11-4 Additivity of Heats of Reactions

The accountant's balance sheet for the water gas system can now be reexamined. This time the heat effects are shown in terms of the experimental values for ΔH.

1. $H_2O(g) + C(s) \longrightarrow CO(g) + H_2(g) \qquad \Delta H_1 = +31.4$ kcal
2. $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_2 = -67.6$ kcal
3. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H_3 = -57.8$ kcal

Addition of these chemical equations leads to the overall equation.

4. $C(s) + O_2(g) \longrightarrow CO_2(g)$

The experimental value for the heat of this reaction, ΔH_4, has been determined.

$$\Delta H_4 = -94.0 \text{ kcal}$$

Notice that $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$

$$\begin{aligned}\Delta H_4 &= 31.4 + (-67.6) + (-57.8)\\ &= 31.4 - 67.6 - 57.8\\ &= -94.0 \text{ kcal}\end{aligned}$$

Figure 11-4 shows the same heat effects in graphical form. This balance sheet is very similar to the one that you obtained in Experiment 26. When a chemical reaction can be expressed as the algebraic sum of two or more reactions, its heat of reaction is the

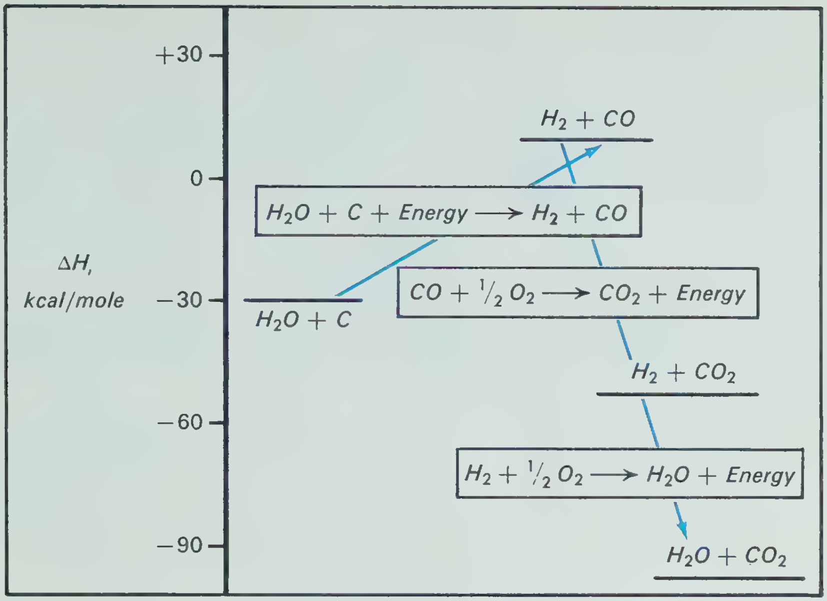


FIGURE 11-4

Heat effects in the manufacture and use of water gas.

algebraic sum of the separate reaction heats. This important generalization has been found applicable to every reaction that has been tested. This principle can be used to predict the heat of reaction for many reactions not included in Table 11-2. For example, find the heat of combustion for nitric oxide, NO.

$$NO(g) + \tfrac{1}{2} O_2(g) \longrightarrow NO_2(g) \qquad \Delta H = ?$$

We look for equations in Table 11-2 that include the compounds NO and NO_2.

$$\tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow NO(g) \qquad \Delta H = +21.6 \text{ kcal}$$

$$\tfrac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H = +8.1 \text{ kcal}$$

Consider a reaction in which the compound NO is a reactant and NO_2 is the product. First, reverse the chemical equation that shows NO as a product. Next obtain the heat for the reversed equation by changing the algebraic sign of ΔH. If 21.6 kcal of heat energy is absorbed when one mole of NO is formed, then 21.6 kcal of heat energy is released when one mole of NO is decomposed in the reversed reaction.

$$NO(g) \longrightarrow \tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g) \qquad \Delta H = -21.6 \text{ kcal}$$

The sign of ΔH changes whenever a chemical equation is reversed in this fashion.

$$NO(g) \longrightarrow \tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g) \qquad \Delta H = -21.6 \text{ kcal}$$

$$\tfrac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H = +8.1 \text{ kcal}$$

Now add, algebraically, the chemical equations and the ΔH values. We obtain the chemical equation for the combustion of NO:

$$NO(g) + \tfrac{1}{2} O_2(g) \longrightarrow NO_2(g) \qquad \Delta H = -21.6 + 8.1$$
$$= -13.5 \text{ kcal}$$

The sign of ΔH is negative. The reaction is exothermic. Heat energy is given off when nitric oxide reacts with oxygen.

EXERCISE 11-1

Convince yourself that ΔH changes sign when a chemical equation is reversed.

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 94.0 \text{ kcal} \qquad \Delta H = ?$$
$$CO_2(g) + 94.0 \text{ kcal} \longrightarrow C(s) + O_2(g) \qquad \Delta H = ?$$

Here is another example, the combustion of methane, CH_4.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad \Delta H = ?$$

Since there are three compounds in this reaction, we must look for the equations in Table 11-2 that include these molecules. We write the equations so that CH_4 is on the left as a reactant. CO_2 and H_2O must appear on the right as products.

$$CH_4(g) \longrightarrow C(s) + 2\,H_2(g) \qquad \Delta H = +17.9 \text{ kcal}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.0 \text{ kcal}$$
$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad \Delta H = -115.6 \text{ kcal}$$

The first equation has been reversed and the sign of ΔH changed. The last equation, including ΔH, has been multiplied by 2 because two moles of H_2O are needed.

Add the chemical equations and the ΔH values.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

$$\Delta H = +17.9 - 94.0 - 115.6$$
$$= -191.7 \text{ kcal}$$

This is also an exothermic reaction. Methane is a very good fuel because of the large amount of heat energy given off when methane burns. The gas used in the burners in most school laboratories is methane.

EXERCISE 11-2

Use the equation $C(s) + O_2(g) \longrightarrow CO_2(g) + 94.0$ kcal to convince yourself that ΔH will double when two moles of carbon are burned.

EXERCISE 11-3

Use values in Table 11-2 to calculate the heat of this reaction:

$$CO(g) + \tfrac{1}{2}\, O_2(g) \longrightarrow CO_2(g)$$

Compare your result with ΔH given for this reaction on page 196.

EXERCISE 11-4

a. Calculate ΔH for one mole of NH_3 reacting with oxygen. Use

$$4\, NH_3(g) + 3\, O_2(g) \longrightarrow 2\, N_2(g) + 6\, H_2O(g)$$

b. Is this reaction exothermic or endothermic?

EXERCISE 11-5

Use values in Table 11-2 to calculate how much heat energy is required to vaporize one mole of H_2O at 25°C.

$$H_2O(l) \longrightarrow H_2O(g)$$

11-5 Conservation of Energy

How many times have you waked up in the morning full of energy? You feel ready to accomplish something that day, whether it is schoolwork or playing football or going to a dance. We all know what the word energy means in these expressions. In this section we will see how scientists use the word energy. Some examples will help.

When gasoline is burned in an automobile engine, part of the potential energy in this fuel is converted into heat energy. The expansion of hot gases moves the engine pistons. A gear system transfers this motion to the wheels and the automobile moves. The amount and kind of fuel used in an automobile engine determine how far (and how fast) the automobile moves.

Water flowing over a dam can drive a paddle wheel. The potential energy of water is transformed into mechanical energy of a rotating wheel. The wheel may be part of a system which generates electricity. Mechanical energy is transformed by a generator into electrical energy. Just think of the ways that electrical energy does work for us: the battery that starts an automobile; the electric motors that move elevators and escalators; the power tools in the wood shop that make sawing and sanding and drilling so much easier for us. The volume of water and the distance it falls over the dam or the kilowatt-hours of electricity generated can be related to the work that can be done.

These examples show that energy can be converted from one form to another. Many careful experiments have led scientists to the view that energy is always conserved. This regularity is called the **Law of Conservation of Energy.** It says that in every experiment so far performed, energy is conserved provided all the different forms of energy are taken into account.

11-6 Comparison of Energy Changes

Chemists interpret energy on the molecular level. In Section 4-4 we saw how the absolute temperature of a gas is directly related to the translational motion of molecules. There are other forms of molecular motion that are important. Let us imagine a molecule as a group of balls hooked together by springs. The balls represent atoms and the springs represent the bonds between atoms. The total kinetic energy for molecules is a result of the kinds of molecular motion shown in Figure 11-5.

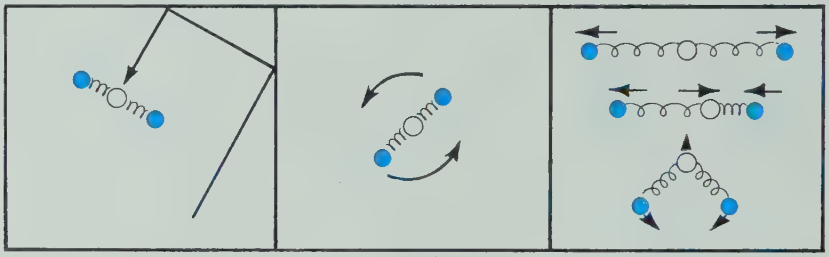


FIGURE 11-5

The three kinds of motion that a molecule may have. Each contributes to the total kinetic energy.

Translational motion of the molecule as a unit. It is this type of motion which is directly related to the absolute temperature of a substance.

Rotational motion of the molecule around its center of mass.

Vibrational motion of the atoms in a molecule toward and away from the center of mass.

Now let us follow what happens at the molecular level as we add thermal energy to a crystalline solid. At first the temperature is very low. This means that the molecular motion about the regular crystal positions is not very large. As energy is added, the temperature of the solid rises. The back-and-forth motion of the molecules increases. At some temperature the kinetic energy of the molecules causes so much random movement that the crystal is no longer stable; the solid melts. A phase change takes place.

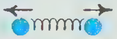
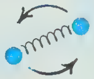
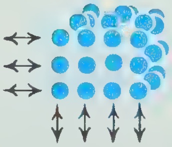
The kinetic energy of the molecules in a liquid is primarily in the form of translation and rotation. Warming the liquid increases the molecular motion. Molecules tend to move about in a random fashion in the liquid. At the boiling temperature, another phase change takes place. The liquid vaporizes and gas molecules move throughout their container.

As more energy is added to the gas, vibration within molecules begins to be an important factor. Ultimately a temperature is reached when the kinetic energy of translation, rotation, and vibration in the molecule becomes comparable to chemical bond energies. Molecules begin to dissociate. Only the simplest molecules are stable at temperatures above several thousand degrees.

If we continue to add thermal energy to our system, a temperature will be reached when the kinetic energy approaches the ionization energies for the atoms. The atoms ionize. This state of matter is called **plasma,** a gas made up of electrons and positive ions. Behavior of plasmas is an important research topic today.

Finally, at a temperature of several million degrees, the kinetic energy is comparable to nuclear binding energies. The particles collide with such tremendous force that nuclear reactions begin. There is good reason to think that many nuclear reactions take place in stars. These reactions are believed to be the source of a star's energy. We will talk about nuclear reactions in Chapter 21.

FIGURE 11-6 Comparison of energy changes.

Source of energy	*Absolute temperature*	*Process occurring*	*State of atoms and molecules*	*Molecular process*
Supernova explosions	°K 100,000,000			
Center of stars	10,000,000	*Nuclear reactions*	$4\,{}_1H \longrightarrow {}_4He$	*Kinetic energy exceeds nuclear energy.*
Plasma	1,000,000	*Ionization of atoms*	$H \longrightarrow H^+ + e^-$	*Kinetic energy exceeds ionization energy.*
	100,000			
Surface of sun	10,000	*Dissociation of molecules*	$H{-}H \longrightarrow H + H$ 	*Vibrational energy exceeds chemical bond energies.*
Bunsen burner	1,000	*Iron melts*		*Molecules move freely and rotate.*
Weather reading *Highest* *Lowest*	100	*Water boils* *Ice melts* *Nitrogen boils*		
	10	*Hydrogen boils* *Hydrogen melts*		*Molecules move back and forth around their equilibrium positions in crystal.*
	1	*Helium boils*		
	0.1			*Almost no motion of molecules in perfect crystals.*

11-7 Review

Every chemical compound has a characteristic mass. Every chemical compound has a characteristic heat content. The heat content of a substance is a measure of the potential energy stored in the substance during its formation. Energy is stored in the bonds and changes when their number and kind are altered in a chemical reaction. The heat effects in a chemical reaction measure the difference between the heat contents of the products and the heat contents of the reactants. Chemists indicate this difference, the heat of reaction, with the symbol ΔH.

If there is an increase in heat content during a chemical reaction ΔH is a positive number. Such a reaction absorbs heat energy from its surroundings. The reaction is **endothermic.**

If there is a decrease in heat content during a chemical reaction, ΔH is a negative number. The reaction gives up heat energy to its surroundings. The reaction is **exothermic.**

Chemists have measured the heats of many reactions. Just as several chemical equations can be added to give an overall equation, so can ΔH values be combined to give the heat of reaction for the overall chemical reaction. This important regularity has been found to apply in every system that chemists have studied.

Energy can be transformed from one type to another. The sum of all types is constant for a fixed system. On a molecular basis, potential energy is present in the bonding arrangement and kinetic energy in the motions of the atoms and molecules.

Questions and Problems for Chapter 11

1

In the process of making water gas, the coke cools. Propose a method of heating this coke.

2

Consider both solid and gaseous fuels. Contrast advantages of using each.

3

Which contains more stored energy (potential energy)?

(a) A burned or an unburned match head
(b) The chemicals a plant needs to make a potato, or the potato
(c) A used or unused photographer's flashbulb
(d) Freshly cut grass or grass that has been through a compost pile

4

The amount of solar radiation received in Arizona is about 180,000 kcal/ft^2/year. How much coke (C) must be burned to CO_2 to produce this amount of heat energy?

5

Which of the following reactions are endothermic?

(a) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g) \quad \Delta H = -57.8 \text{ kcal}$
(b) $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \longrightarrow NO(g) \quad \Delta H = +21.6 \text{ kcal}$
(c) $NH_3(g) \longrightarrow \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \quad \Delta H = +11.0 \text{ kcal}$
(d) $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g) + 11.0 \text{ kcal}$
(e) $\frac{1}{2} N_2(g) + O_2(g) + 8.1 \text{ kcal} \longrightarrow NO_2(g)$

6

What is the minimum energy required to synthesize one mole of nitric oxide, NO, from the elements?

7

How much energy is liberated when 0.100 mole of H_2 at 25°C and 1 atmosphere is combined with enough $O_2(g)$ to make liquid water at the same conditions?

8

How much energy is consumed in the decomposition of 5.0 grams of $H_2O(l)$ at 25°C and 1 atmosphere into its gaseous elements at the same conditions?

9

Which one of the following statements is FALSE as applied to this equation?

$$H_2(g) \rightleftharpoons H(g) + H(g) \qquad \Delta H = 103.4 \text{ kcal}$$

(a) The positive ΔH means the reaction is endothermic.
(b) Two grams of $H(g)$ contain more energy than 2 grams of $H_2(g)$.
(c) Mass for mass, $H(g)$ would be a better fuel than $H_2(g)$.
(d) The spectrum of $H_2(g)$ is the same as the spectrum of $H(g)$.

10

To change the temperature of a particular calorimeter and the water it contains by one degree requires 1550 calories. The complete combustion of 1.40 grams of ethylene gas, $C_2H_4(g)$, in the calorimeter causes a temperature rise of 10.7 degrees. Find the heat of combustion per mole of ethylene.

11

Given

$$3\,C(s) + 2\,Fe_2O_3(s) + 110.8 \text{ kcal} \longrightarrow 4\,Fe(s) + 3\,CO_2(g)$$

Rewrite the equation, using one mole of carbon and the ΔH notation.

12

Given

$$\tfrac{1}{2}\,H_2(g) + \tfrac{1}{2}\,Br_2(l) \longrightarrow HBr(g) \qquad \Delta H = -8.60 \text{ kcal/mole HBr}$$

Rewrite the equation for one mole of hydrogen gas and include the heat effect as a term in the equation.

13

Using Table 11-2, calculate the heat of burning ethane in oxygen to give CO_2 and water vapor.

Answer. $\Delta H = -341$ kcal/mole C_2H_6.

14

Given

$$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.50 \text{ kcal}$$

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.05 \text{ kcal}$$

Find ΔH for the manufacture of diamond from graphite.

$$C(\text{graphite}) \longrightarrow C(\text{diamond})$$

Is heat absorbed or evolved as graphite is converted to diamond?

15

The "thermite reaction" is spectacular and highly exothermic. It involves the reaction between Fe_2O_3, ferric oxide, and metallic aluminum. The reaction produces white-hot, molten iron in a few seconds. Given:

$$2\,Al + \tfrac{3}{2}\,O_2 \longrightarrow Al_2O_3 \qquad \Delta H_1 = -400 \text{ kcal/mole}$$

$$2\,Fe + \tfrac{3}{2}\,O_2 \longrightarrow Fe_2O_3 \qquad \Delta H_2 = -200 \text{ kcal/mole}$$

Determine the amount of heat liberated in the reaction of 1 mole of Fe_2O_3 with Al.

Answer. $\Delta H = -200$ kcal/mole Fe_2O_3.

16

How much energy is released in the manufacture of 1.00 kg of iron by the "thermite reaction" mentioned in Problem 15?

17

How many grams of water could be heated from 0°C to 100°C by the heat liberated per mole of aluminum oxide formed in Problem 15?

18

Which would be the better fuel on the basis of the heat released per mole burned, nitric oxide, NO, or ammonia, NH_3? Assume the products are $NO_2(g)$ and $H_2O(g)$.

19

What is the minimum energy required to produce one mole of sulfur dioxide from sulfuric acid?

$$H_2SO_4(l) \longrightarrow SO_2(g) + H_2O(g) + \tfrac{1}{2}\,O_2(g)$$

Answer. $\Delta H = +65$ kcal/mole $SO_2(g)$.

20

The heat of reaction for the formation of MgO(s) from the elements is −144 kcal/mole of MgO(s). How much heat is liberated when magnesium reduces the carbon in CO_2 to free carbon? See Table 11-2.

Answer. $\Delta H = -97$ kcal/mole MgO.

21

SO_2 can be combined with oxygen to give SO_3. The molar heat of reaction is −23.0 kcal/mole SO_2. Calculate ΔH to form one mole of SO_3 from S_8 and O_2.

22

The formation of liquid methanol, CH_3OH, from elements releases 152.6 kcal/mole CH_3OH. Calculate ΔH for combustion of one mole of methanol to CO_2 and H_2O.

23

How much water can be boiled by using the heat from completely burning one mole of carbon?

(a) If the water is at 100°C
(b) If it is at 0°C and must be warmed to 100°C first

24

Combustion of acetylene, C_2H_2, is represented by

$$C_2H_2(g) + \tfrac{5}{2}\,O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l) \qquad \Delta H = -312 \text{ kcal/mole}$$

What is ΔH for forming one mole of acetylene from carbon and hydrogen?

25

Which gives more heat on burning, a mole of acetylene or a mole of ethane? See Problem 24 and Table 11-2 for data.

26

In Chapter 10, the family of saturated hydrocarbons was represented by the formula C_nH_{2n+2}. Each successive member of this family adds a $-CH_2-$ unit. Use the values in Table 11-2 and the equation

$$4\,C(s) + 5\,H_2(g) \longrightarrow C_4H_{10}(g) \qquad \Delta H = -29.8 \text{ kcal}$$

to estimate the ΔH for the formation of one mole of pentane, C_5H_{12}, from the elements. (Hint: calculate the change in ΔH for each additional CH_2 unit.)

27

Why is the Law of Conservation of Energy considered to be valid?

28

What do you think would happen in scientific circles if a clear-cut, well-verified exception was found to the Law of Conservation of Energy as stated in the text, page 201?

29

Is energy conserved when a ball of mud is dropped from your hand to the ground? Explain your answer.

30

List several things that can be done to a steel spring that will increase the energy stored in it.

31

What becomes of the energy supplied to water molecules as they are heated in a closed container from 25°C to 35°C?

32

Outline the events and associated energy changes that occur on the molecular level when steam at 150°C and 1 atmosphere pressure loses energy continually until it finally becomes ice at −10°C.

The Rates of Chemical Reactions

12

An iron nail reacts slowly in air as it rusts. White phosphorus bursts into flame when exposed to air. Candle wax burns only after we light the wick of the candle. These reactions with the oxygen in air take place at different rates. When we know the factors that influence the rate of a chemical reaction, we can control the reaction. In this chapter we will study the rates of chemical reactions by finding what factors influence them.

When hydrogen iodide gas is heated to 400°C, hydrogen and iodine are the products of the reaction.

$$2\,HI(g) \longrightarrow H_2(g) + I_2(g)$$

The purple color of iodine vapor gradually increases as the reaction proceeds. We can calculate the rate of the reaction by determining the color change during a certain time interval. Since H_2 and HI are colorless, the color change indicates the change in iodine concentration. The rate of the reaction is given by the equation:

$$\text{Rate} = \frac{\text{change in iodine concentration}}{\text{time interval}}$$

FACTORS AFFECTING REACTION RATES

12-1 The Nature of the Reactants

You can draw on your experience in the laboratory to compare rates of different chemical reactions. In Experiment 24 you made qualitative comparisons of the rates of these reactions:

$$5\,Fe^{2+} + MnO_4^{-} + 8\,H^{+} \longrightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O \qquad \text{fast}$$

$$5\,C_2O_4^{2-} + 2\,MnO_4^{-} + 16\,H^{+} \longrightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O \quad \text{slow}$$

Both ferrous ion, Fe^{2+}, and oxalate ion, $C_2O_4{}^{2-}$, react with permanganate ion, $MnO_4{}^-$, at room temperature.* Yet there is a large difference in the rates of these reactions. The purple color of the permanganate ion disappeared much more rapidly in the first reaction. The concentrations of permanganate and hydrogen ions were the same at the start of your experiments. In addition, the temperature was approximately the same. Therefore, the difference in the rates must be associated with specific properties of Fe^{2+} and $C_2O_4{}^{2-}$.

When colorless nitric oxide escapes from a test tube into the air, the reddish-brown color of nitrogen dioxide gas forms very rapidly. When carbon monoxide in the exhaust fumes of an automobile mix with air, the reaction to form carbon dioxide is very slow.

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \qquad \text{fast at 25°C}$$

$$2\,CO + O_2 \longrightarrow 2\,CO_2 \qquad \text{very slow at 25°C}$$

The form of these balanced equations is identical. Clearly the difference in reaction rates must depend on the properties of NO and CO. The determination of the molecular properties which affect rate behavior is an important frontier of chemistry.

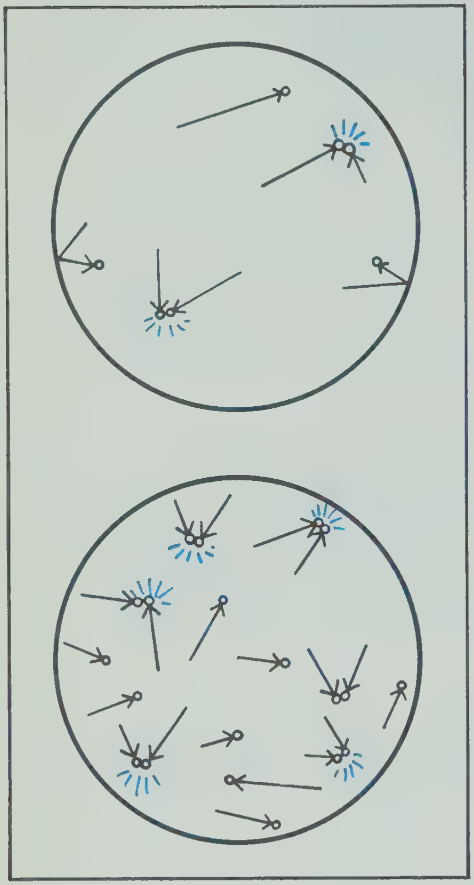


FIGURE 12-1

Number of collisions depends on concentration.

12-2 Effect of Concentration: Collision Theory

In Experiment 28 you studied the rate of the reaction between peroxydisulfate ion, $S_2O_8{}^{2-}$, and iodide ion, I^-. You found that the reaction rate increased when you increased the concentration of either reactant. According to the molecular view of matter, we can assume that two molecules must come close together to react. Chemical reactions depend on collisions between the reacting molecules. This model, used to explain reaction rates, is called the **collision theory.** It helps us understand the effect of concentration on reaction rate. When the concentration of a reactant increases, the number of molecules or ions in a given volume increases. The number of collisions each second goes up. We would expect the reaction rate to increase.

EXERCISE 12-1

Assume that you have 1 mole of HI gas in a 1-liter flask at 400°C.

(a) What is the concentration of HI, in moles per liter?

(b) What would the concentration be if the same amount of HI were put in a 500 ml flask?

(c) Predict whether the reaction will be faster in (a) or (b).

---

* In general, we will no longer use the designation (aq) to indicate that ionic and molecular species are hydrated.

EXERCISE 12-2

Reactions between gases and solids are very important, particularly in many industrial processes. On the reasonable assumption that gas molecules must collide with the solid for reaction to occur, compare the rates of reaction in these three situations. The same mass of solid is considered in each instance.

Gas molecules collide with solid

(a) made of cubes 1 cm on edge.
(b) made of cubes 10^{-1} cm on edge.
(c) made of cubes 10^{-3} cm on edge.

12-3 Reaction Mechanisms

Molecules or ions must collide for a chemical reaction to occur. The equation for the reaction between Fe^{2+} and MnO_4^- indicates that fourteen ions react with each other.

$$5\,Fe^{2+} + MnO_4^- + 8\,H^+ \longrightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$$

The balanced equation seems to suggest that all of these ions would have to collide at the same time. The probability of that happening is very small. The rate of a chemical reaction which depends on so many particles coming together at one time would be very small. And yet you have seen in the laboratory that this reaction is fast. It must proceed by a series of reactions or steps each of which involves more probable collisions. Chemists call such a series of reactions the **reaction mechanism.**

Consider another, less complicated reaction than the ferrous-permanganate reaction. You have studied the reaction between peroxydisulfate ion and iodide ion in some detail.

$$S_2O_8^{2-} + 2\,I^- \longrightarrow 2\,SO_4^{2-} + I_2$$

Quantitative studies of the rate for this reaction show that doubling concentration of the peroxydisulfate ion doubles the rate of the reaction. Doubling the concentration of the iodide ion also doubles the rate of the reaction. Yet in the balanced equation, two iodide ions are needed for one peroxydisulfate ion. Why does a change in iodide concentration have the same effect as an equal change in peroxydisulfate concentration?

An explanation can be given by proposing that this reaction takes place in two steps.

$$S_2O_8^{2-} + I^- \longrightarrow SO_4^{2-} + SO_4I^- \qquad \text{slow}$$
$$SO_4I^- + I^- \longrightarrow SO_4^{2-} + I_2 \qquad \text{fast}$$

First, notice that adding these equations gives the overall equation.

$$S_2O_8^{2-} + 2\,I^- \longrightarrow 2\,SO_4^{2-} + I_2$$

For any proposed reaction mechanism, we must always be able to add up all of the separate steps to give the balanced equation for the observed reaction.

Second, observe that each reaction requires a collision of only two ions. We can see that the first step is the "bottleneck" in the reaction between peroxydisulfate and iodide ions. Almost as soon as the ion SO_4I^- forms, it disappears in the second, fast reaction. The rate of I_2 formation is determined by the rate of the slow reaction in the sequence. The slow reaction in a reaction mechanism is called the **rate-determining step.** Now we can understand why peroxydisulfate and iodide are equally effective in increasing the reaction rate. One peroxydisulfate ion collides with one iodide ion in the slow rate-determining reaction. Doubling the concentration of one reactant is just as effective as doubling the concentration of the other.

EXERCISE 12-3

Imagine five people working together to wash dishes. The first two clear the table and hand the dishes to the third person. He washes them and hands them on. The last two persons dry and stack them. Which step is likely to be the rate-determining step? Discuss how the rate of the overall process would be affected if a sixth person joined the group (a) as a table clearer; (b) as a second dishwasher; (c) as a dish dryer.

12-4 Effect of Temperature: Collision Theory

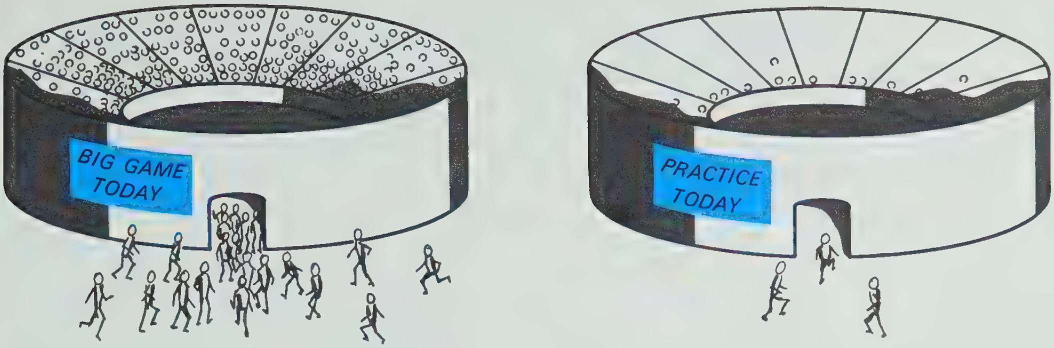
In the laboratory you observed that temperature influences the rate of a chemical reaction. Raising the temperature speeds up the reaction between $S_2O_8^{2-}$ and I^-. The same effect is observed in the reaction between air and methane in your laboratory burner. A match "lights" the methane by raising its temperature. The combustion reaction releases enough heat to keep the temperature high. The reaction continues at a reasonable rate. Raising the temperature speeds up the reaction.

Two questions come to mind:

> "Why does a temperature rise increase the rate of a reaction?"
> "Why does a temperature rise have such a large effect?"

Perhaps the collision theory model will lead to answers for these questions.

We can calculate for a mixture of carbon monoxide and air under normal conditions that a particular CO molecule collides with an O_2 molecule about once in 10^{-9} second. Every second, a CO molecule collides with 10^9 O_2 molecules. Yet virtually no reaction occurs at room temperature. Most collisions between molecules are not effective. Chemists have learned that chemical reactions occur only when collisions have sufficient energy to cause a rearrangement of atoms. We can understand this if we think of collisions between cars. Frequently, in slowly moving traffic, there are gentle bumps from the



Compare chances of collision

car behind. No damage is done to the cars. Occasionally a high-speed collision occurs. High-energy collisions cause auto damage. High-energy molecular collisions cause the "molecular damage" called a chemical reaction.

In Section 4-6 we described an experiment to measure the kinetic energies for molecules. That experiment showed that there is a distribution of molecular energies. A few molecules travel at very high speeds. They have high kinetic energy. If one of these molecules collides with another molecule, we would expect "molecular damage" to take place. Most molecules in the sample have much lower speed and energy. The distribution curve at temperature T_1, showing the number of molecules having a particular energy, is drawn in Figure 12-2. This curve will be useful in discussing the effect temperature has on the rate of a chemical reaction. Let us propose that chemical reactions take place only if the *two colliding molecules bring enough energy to the collision* so that rearrangement of atoms to form new molecules occurs. The minimum amount of energy is called the **threshold energy,** E. A vertical line is drawn in Figure 12-2 to indicate this energy. The shaded area to the right of this line shows us the fraction of molecules with energy greater than E. Remember that it is not necessary for each reacting molecule to have energy greater than the threshold energy. If a low-energy molecule collides with a very high energy molecule, reaction may occur.

At the temperature T_1, not many molecules have energies greater than the threshold energy. Not many collisions involve energies greater than the threshold energy. Very few of the collisions lead to chemical reaction. What happens when the temperature is increased to T_2? The distribution curve changes shape. It flattens and spreads out as shown in Figure 12-2. The average speed of the molecules is greater at the higher temperature. There are many more molecules now that have kinetic energy greater than the threshold energy, E. Many more of the collisions involve energy greater than E. Therefore, the reaction rate is much greater at a higher temperature.

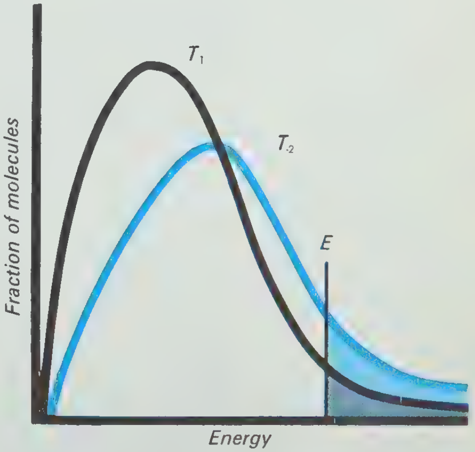


FIGURE 12-2

Energy distributions at two temperatures. Number of molecules with energy greater than E is much larger at the higher temperature, T_2.

12-5 Activation Energy

Imagine someone trying to roll a bowling ball up a very steep hill. On most tries, the bowling ball slows down and stops before it gets

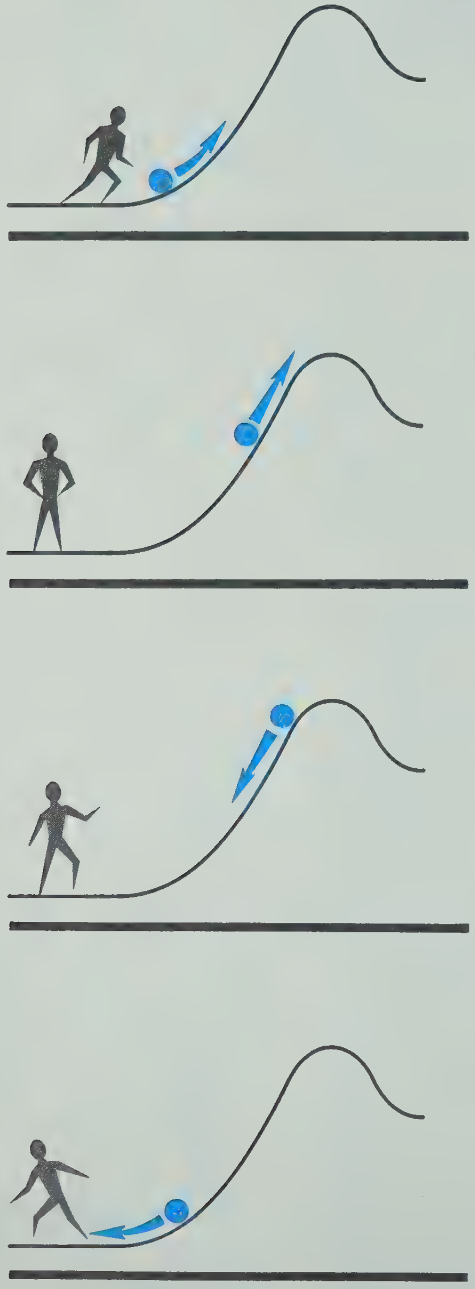


FIGURE 12-3

Insufficient energy; ball returns to original level.

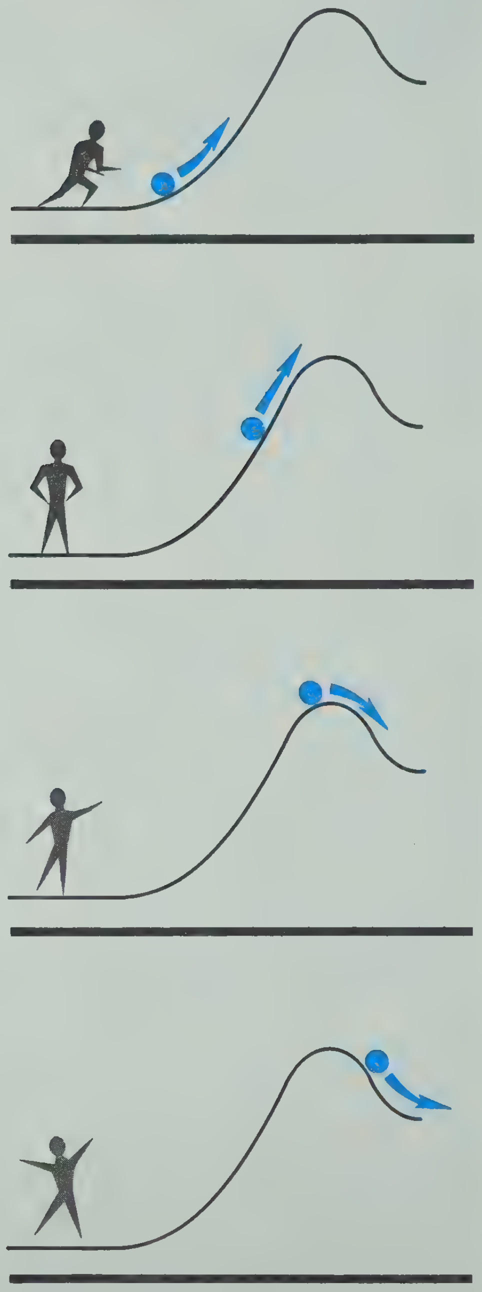


FIGURE 12-4

Sufficient energy; ball goes over to a new level.

to the top of the hill. Then it rolls back down on the same side of the hill. The kinetic energy of the bowling ball is converted to potential energy as the ball slows down. Look at Figure 12-3 to see what happens. Only occasionally does the bowler give the ball enough kinetic energy so that it gets to the top of the hill and rolls down the other side. A successful try is shown in Figure 12-4.

We can picture a similar situation for molecules in a chemical reaction. During molecular collisions, atoms can take up new bonding arrangements that have more potential energy than either the reactants or the products. These atomic arrangements have high potential energy like the bowling ball at the top of the hill. Our model, collision theory, suggests there is a potential energy hill or barrier between the reactant and product molecules in a chemical reaction. In Figure 12-5 we show the distribution curve for the kinetic energy of molecular collisions placed next to the potential energy hill for a chemical reaction. To react, molecules must collide with enough energy to assume the high-energy atomic configuration represented by the top of the hill. With less energetic collisions, the molecules do not react. Several values are marked on the energy distribution curve with dots. If molecular collisions having those energies occurred, the system could reach the corresponding dots on the potential energy diagram. Quite obviously these collisions are not successful ones.

The energy barrier shows the minimum threshold energy, *E*. Chemists have given *E* the name **activation energy.** The atomic configuration at the top of the energy barrier is a "molecule" called the **activated complex.** At first, this molecule may seem unusual to you. It has a very short lifetime and gets rid of its high potential energy by breaking apart, forming either the reactants or the products. Either of these atomic arrangements has less potential energy than the activated complex.

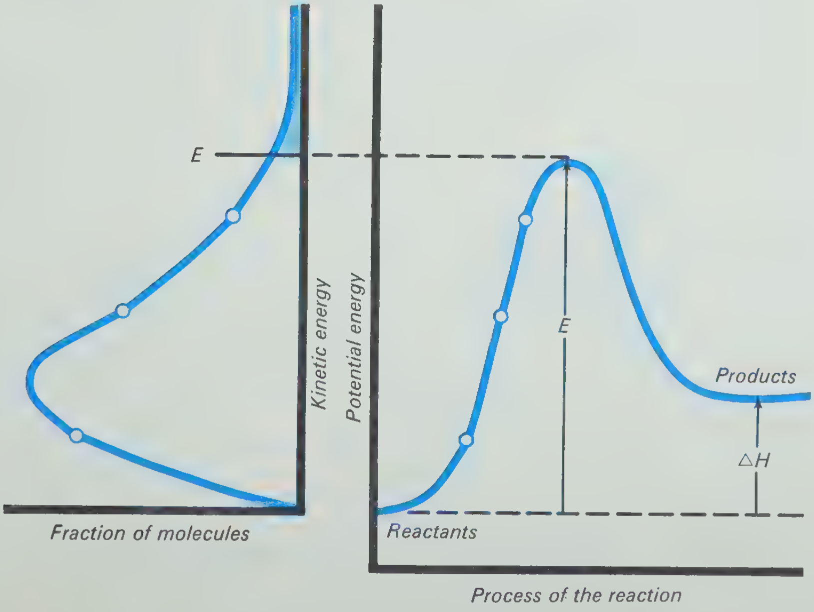


FIGURE 12-5

Comparison of kinetic energy distribution curve with activation energy diagram. Only a small fraction of molecules have sufficient kinetic energy to reach the top of the potential energy hill.

Figures 12-6 to 12-10 will help you visualize what happens when two hydrogen iodide molecules react to form hydrogen and iodine. Potential energy is plotted vertically and the horizontal direction shows the progress of the reaction. The position of the dot in each of these figures represents the potential energy for the entire system. The most favorable geometry for these collisions is shown. This geometry corresponds to the smallest possible value for E in the reaction.

12-6 The Heat of Reaction

The reaction between HI molecules is endothermic. The potential energy or heat content of the products, H_2 and I_2, is greater than the heat content of the reactants. Figure 12-11 shows the ΔH for this reaction, 2.4 kcal per mole of hydrogen formed. The heat of reaction, ΔH, depends only on the energy difference between the reactants and the products of a reaction. The heat of the reaction does not depend on the height of the activation barrier.

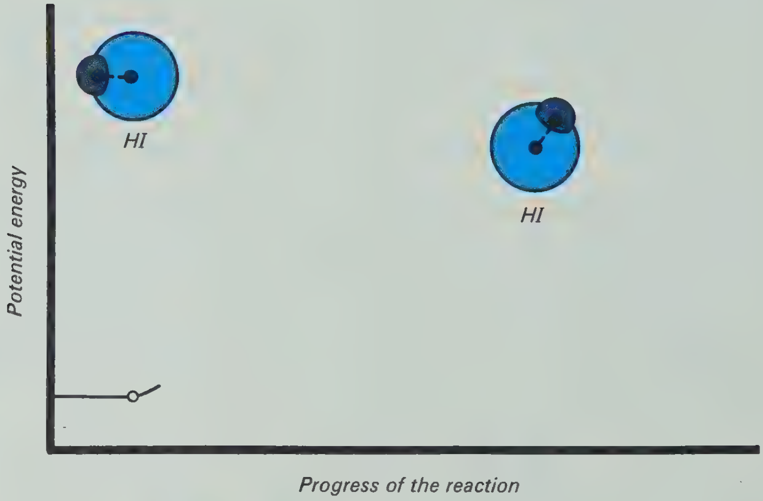


FIGURE 12-6

The two HI molecules are so far apart they do not have any appreciable interactions. The potential energy of the system is constant and is represented by the dot on the horizontal line on the left. The HI molecules have kinetic energy of translation and rotation.

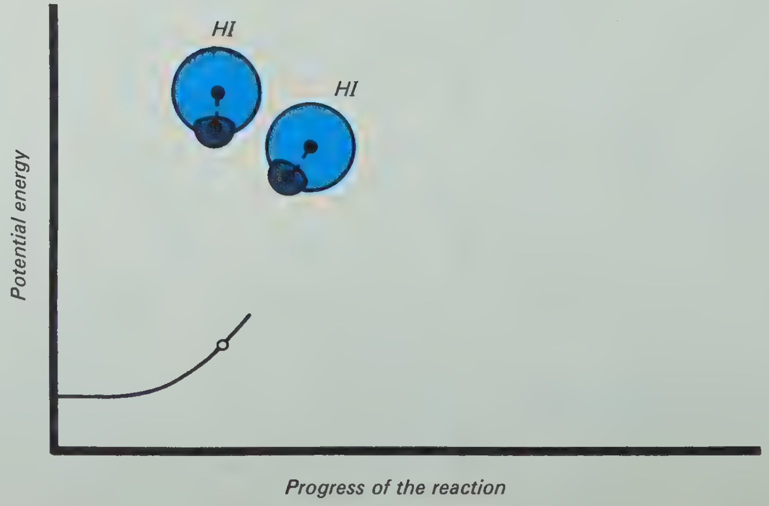


FIGURE 12-7

As the molecules get closer to each other, they interact and the four atoms begin to take on a new arrangement. The potential energy of the system increases. This increase in potential energy must be compensated by a decrease in kinetic energy of the HI molecules. The molecules slow down. If the two molecules are not approaching each other with sufficient combined energy, they rebound and separate. The system goes back to the one shown in Figure 12-6. However, if the molecules approach with a large amount of kinetic energy, the situation develops as shown in Figure 12-8.

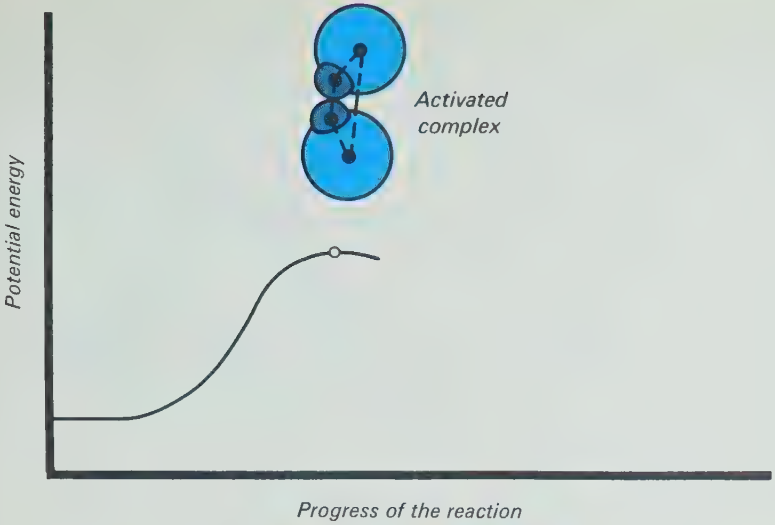

Activated
complex
Potential energy
Progress of the reaction

FIGURE 12-8

The molecular collision involves enough energy to bring the four atoms close enough to form a new molecule, H_2I_2. Chemists call this molecule the activated complex. It is an unusual molecule in that it does not exist for very long. This arrangement of the four atoms has a large amount of potential energy. A large fraction of kinetic energy that the HI molecules started with has been transformed into potential energy of the H_2I_2 molecule. This molecule can either re-form the reactants, HI and HI, Figure 12-6, or it can form the product molecules, H_2 and 2 I. Go on to Figure 12-9 to see this.

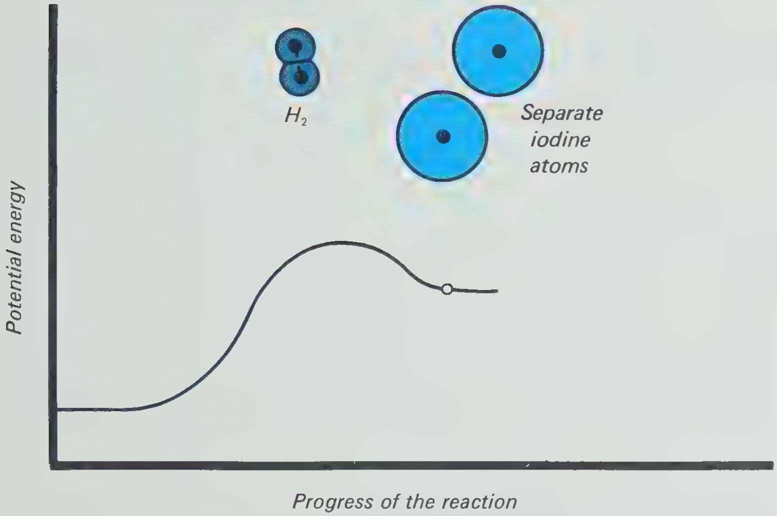

H₂
Separate
iodine
atoms
Potential energy
Progress of the reaction

FIGURE 12-9

If the reaction proceeds, two I atoms and one H_2 molecule form. The high potential energy of the activated complex, H_2I_2, appears as kinetic energy of translation and rotation in H_2 and in 2 I. As the products move apart, they interact less and less. The potential energy level on the right is characteristic of two hydrogen atoms and two iodine atoms arranged as H_2 and 2 I. The potential energy of the system is still very high because of the energy of the two iodine atoms.

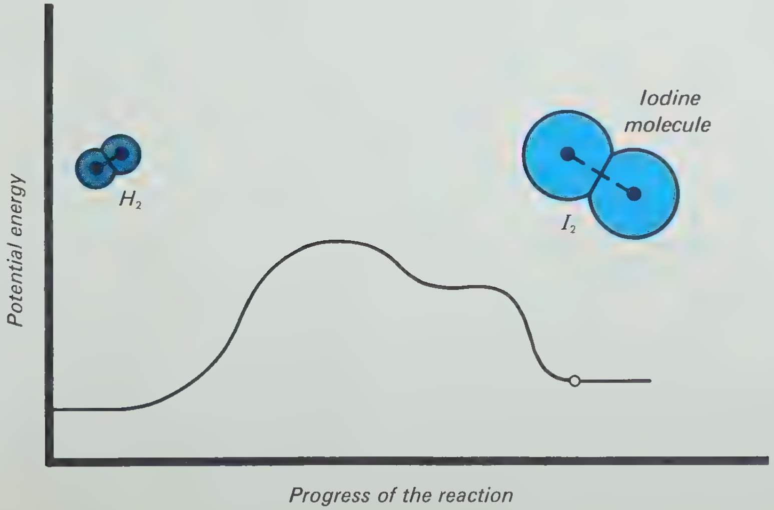

Iodine
molecule
H₂
I₂
Potential energy
Progress of the reaction

FIGURE 12-10

The iodine atoms have combined to form an iodine molecule. The potential energy level on the right is characteristic of two hydrogen atoms and two iodine atoms arranged as one H_2 molecule and one I_2 molecule. This level is higher than the initial potential energy level for the system. Almost all of the kinetic energy brought into the collision is now in the form of the translation and rotation of the products.

Let's reverse our series of pictures. We can trace the reaction between H_2 and I_2 by starting with Figure 12-10 and working back to Figure 12-6. All of the ideas we have been discussing would be applicable to this reaction.

$$\begin{aligned} I_2 &\rightleftarrows 2\,I \\ H_2 + 2\,I &\rightleftarrows H_2I_2 \qquad \text{(activated complex)} \\ H_2I_2 &\rightleftarrows HI + HI \end{aligned}$$

Iodine molecules dissociate, giving iodine atoms. The activated complex forms if the hydrogen molecule and the two iodine atoms collide with enough energy to reach the top of the potential energy barrier.

If we focus our attention on the left half of Figure 12-11, an important relation between activation energy and ΔH is revealed. The energy arrows show that

$$E_F = \Delta H + E_R$$

When two of these quantities are known from experiments, it is easy to calculate the third. In this example

$$2\,HI \longrightarrow (H_2I_2) \longrightarrow H_2 + 2\,I \qquad \Delta H = 38.5 \text{ kcal}$$
$$E_F = 43.8 \text{ kcal}$$

Therefore $E_R = 43.8 - 38.5 = 5.3$ kcal

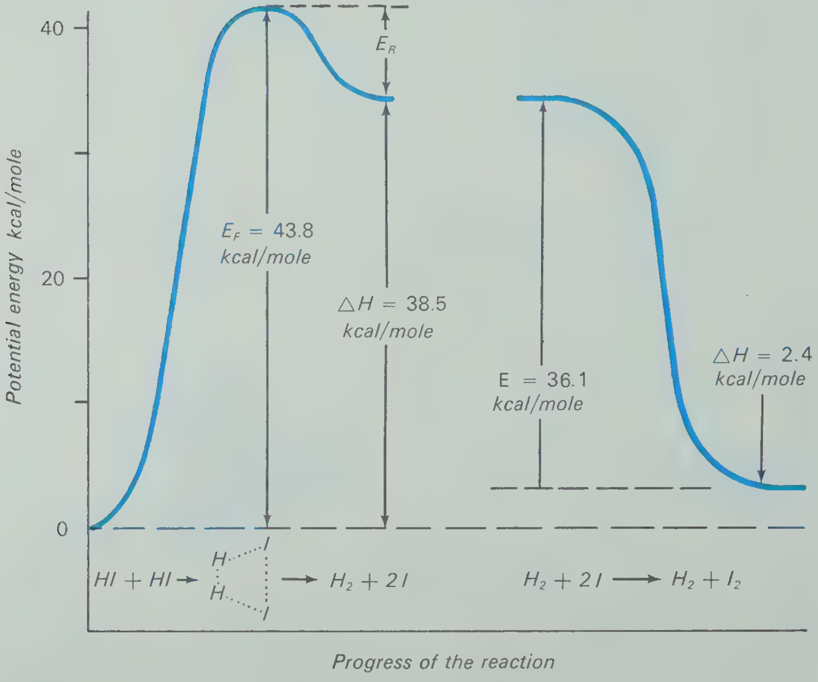


FIGURE 12-11

Activation energy diagram for the reaction $2\,HI(g) \longrightarrow H_2(g) + I_2(g)$.

12-7 Action of Catalysts

Many reactions that take place slowly can be made to take place more rapidly by the introduction of other substances. These substances are called **catalysts.** They are not used up in the reaction.

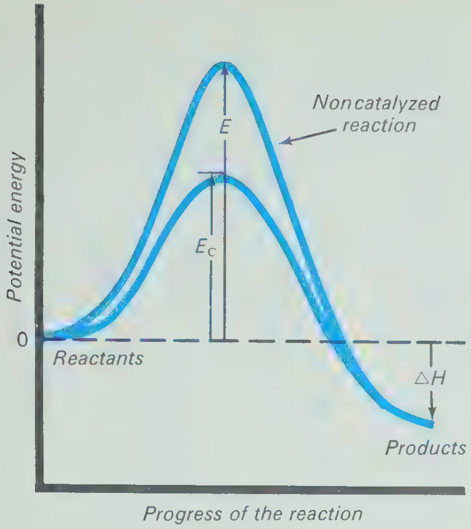


FIGURE 12-12

Activation energy diagram for catalyzed and noncatalyzed reactions.

You have seen several examples of catalysis in your laboratory work. The reaction between $C_2O_4^{2-}$ and MnO_4^- is speeded up by addition of the catalyst, Mn^{2+}. Cupric ion, Cu^{2+}, acts as a catalyst for the reaction between $S_2O_8^{2-}$ and I^- ions.

Let's go back to the fellow trying to roll bowling balls over a hill. Suppose rain washed away part of the hilltop and somehow made a smooth path. The bowler would have an easier time. He would not have to work so hard rolling the bowling ball to the other side of the hill. The newly made path, or ravine, offers a low-energy route. More bowling balls would get to the other side of the hill in a certain period of time. Fewer bowling balls would roll back down the hill. Of course, the bowler may occasionally want to see if he is still strong enough to roll the bowling ball by the first path, over the top of the hill. Both routes are possible. In any case, more bowling balls get to the other side of the hill per unit of time.

We can imagine a similar situation when thinking about catalysts. Somehow the catalyst provides a "molecular ravine," a low-energy path between the reactants to the products. More particles can get over the new lower-energy barrier per unit of time. The reaction proceeds at a greater rate. The effect of the catalyst on the activation energy is shown in Figure 12-12. The catalyzed route has a lower activation energy, E_C, than the original, noncatalyzed path. The new reaction path corresponds to a new reaction mechanism. The molecules combine with the catalyst to form a different activated complex. Notice that the activation energy for the reverse reaction is lowered exactly the same amount as for the forward reaction. A catalyst speeds up the reverse reaction just as much as it speeds up the forward reaction. On the other hand, the value of ΔH for the reaction does not change when a catalyst is present. This fact is illustrated in Figure 12-12. The energy levels for reactants and products are not changed by the catalyst. Only the reaction mechanism and the activation energy change.

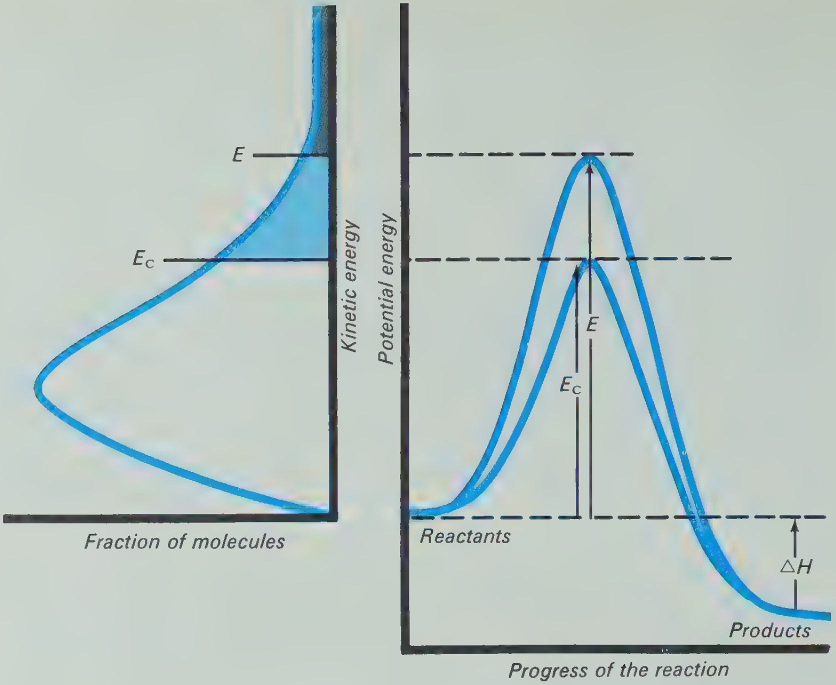


FIGURE 12-13

Comparison of energy curves for a catalyzed and noncatalyzed reaction path. A larger fraction of molecules have sufficient kinetic energy to reach the top of the lower potential energy hill. *However,* ΔH does not change.

Before discussing some important chemical reactions, let's look at the arrangement of energy diagrams shown in Figure 12-13. The curve showing distribution of kinetic energy and the potential energy diagram are placed next to each other. Two horizontal lines represent the activation energy for the catalyzed and noncatalyzed reactions. The shaded areas indicate the number of molecules having kinetic energy greater than E_c and E. There are many molecules having energy greater than E_c. Only a few molecules have energy greater than E. The catalyzed reaction has a higher reaction rate than the noncatalyzed reaction.

12-8 Some Reaction Mechanisms

A. Molecular Inversion

The reaction between methyl bromide and hydroxide ion is moderately slow at 25°C.

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

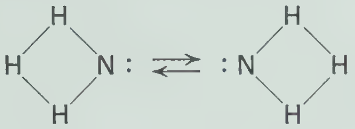
An increase in hydroxide or methyl bromide concentrations has the same effect in speeding up the reaction. A collision between one hydroxide ion and one methyl bromide molecule is the rate-determining step in the reaction. The molecular models in Figure 12-14 help us follow the reaction.

Several points are worth mentioning:

1. The hydroxide ion approaches from one side of the CH_3Br molecule. The bromide ion leaves from the opposite side.

2. The potential energy of the activated complex is very high. The atoms have taken up unstable positions during the short lifetime of the activated complex.
3. The methyl group has been turned inside out in this reaction, like an umbrella in a strong wind. This is the reason the reaction is called an **inversion.**

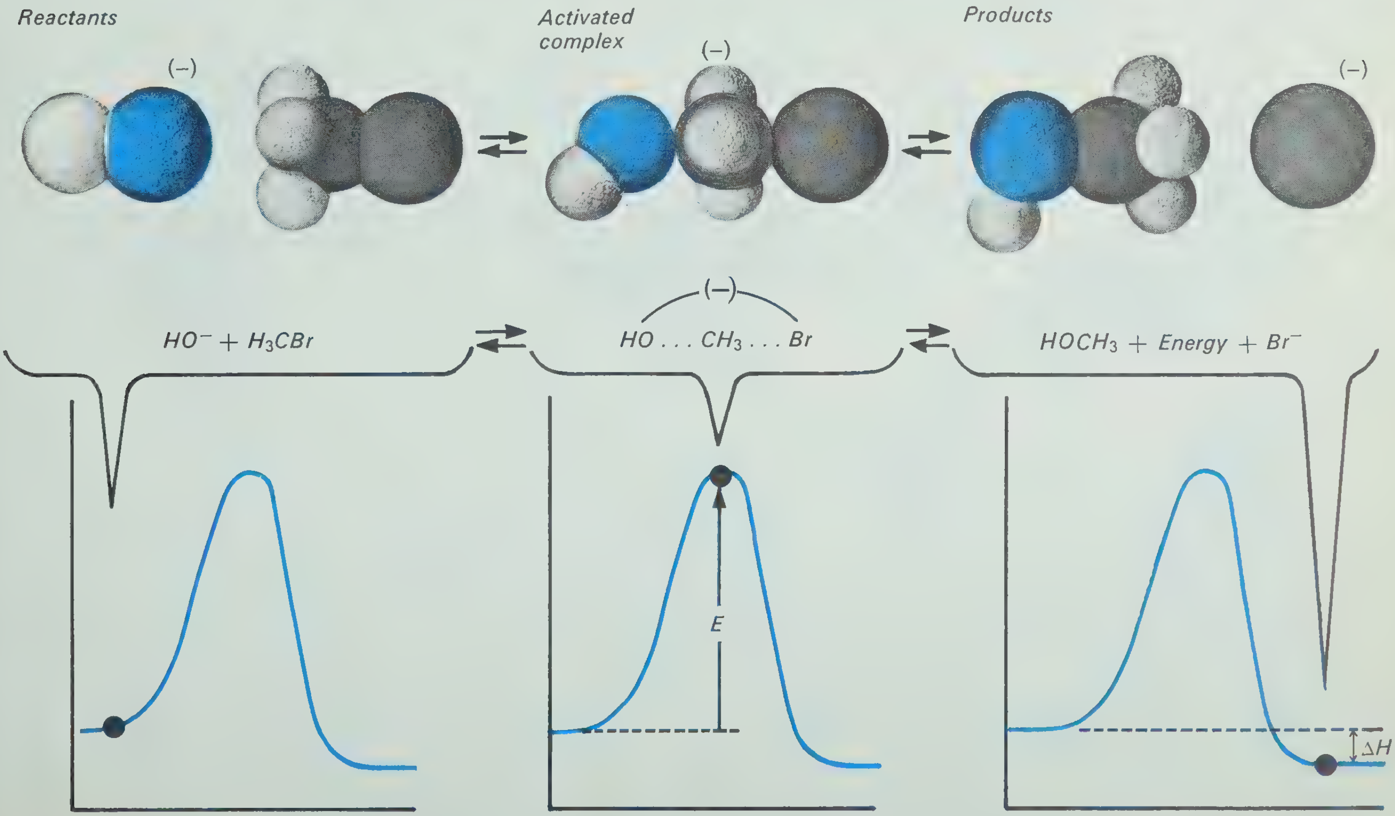
This mechanism applies to many reactions. One vibrational motion of the NH_3 molecule is an inversion. The number of times an NH_3 molecule turns inside out, 2.3780×10^{10} times each second, is known with high precision. This vibration is the basis for very precise time measurements.



B. Chain Reactions

The reaction between H_2 and I_2 is slow. Rate measurements lead to a reaction mechanism based on one H_2 molecule colliding with two I atoms. You might expect the $H_2 + Cl_2$ reaction to be similar. However, we find the reactions are very different. The hydrogen and

FIGURE 12-14 The mechanism and potential energy diagram for the reaction $CH_3Br + OH^- \rightleftarrows CH_3OH + Br^-$.



chlorine reaction is very fast, almost an explosion. The reaction can be triggered at room temperature by shining light on a mixture of H_2 and Cl_2. The mechanism for this reaction appears to be this set of steps:

$$\begin{aligned} Cl_2 + \text{light} &\rightleftarrows 2\,Cl \\ Cl + H_2 &\longrightarrow HCl + H \\ H + Cl_2 &\longrightarrow HCl + Cl \\ Cl + H_2 &\longrightarrow HCl + H \\ H + Cl_2 &\longrightarrow HCl + Cl \\ \hline \text{Many } H_2 + \text{many } Cl_2 &\longrightarrow \text{many } HCl \end{aligned}$$

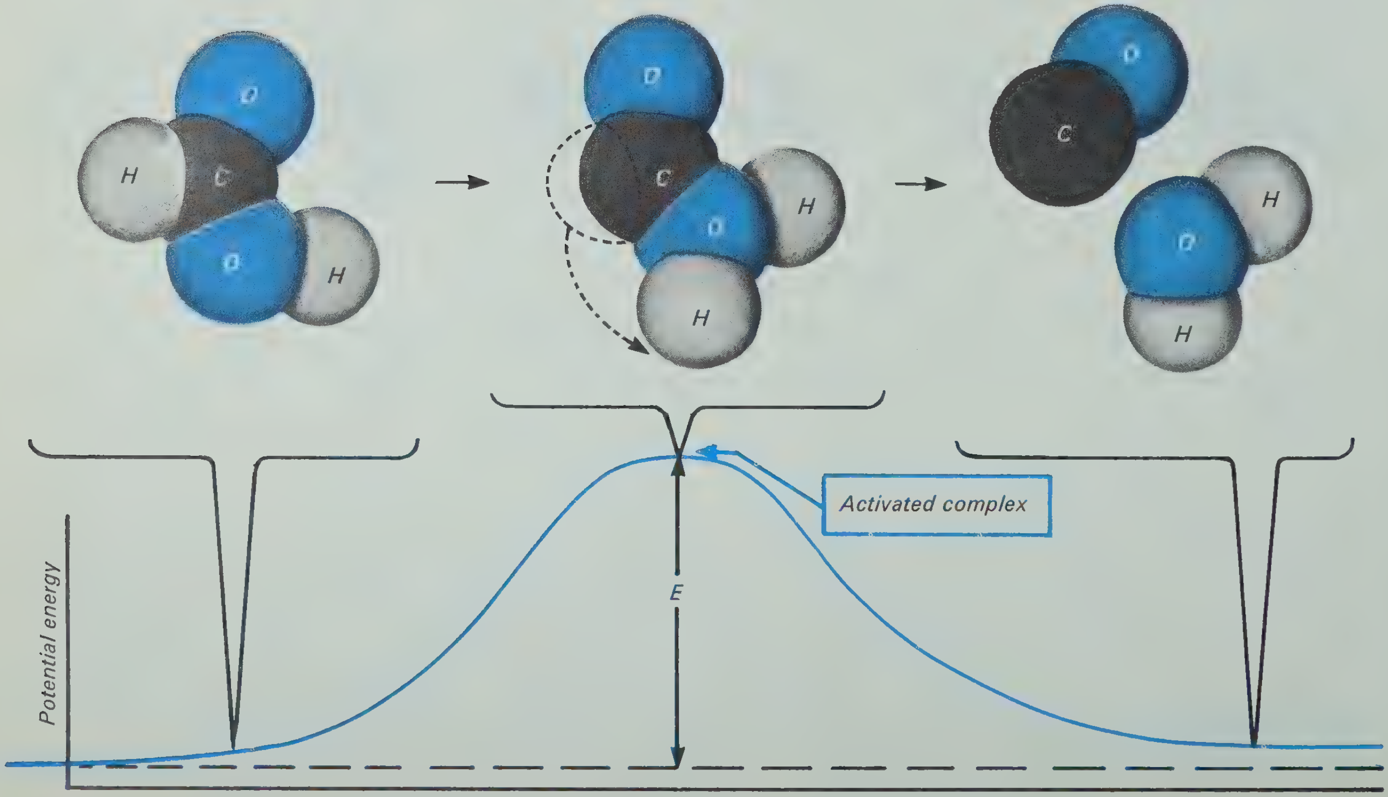
One Cl atom sets off a chain reaction. A large number of H_2 and Cl_2 molecules react almost instantaneously. A large amount of energy is liberated in a very short time. The temperature and pressure of the system increase rapidly.

There are many important examples of chain reactions in which very large molecules can be built in a controlled fashion. We will discuss some of these in Chapter 18.

C. Acid Catalysis

In all cases of catalysis, the catalyst acts by providing a lower energy path for a reaction. Without the catalyst these paths would

FIGURE 12-15 Mechanism and activation energy diagram for noncatalyzed decomposition of formic acid.



not be available. Some place, in the new reaction mechanism, the catalyst is regenerated. One of the most important catalysts is the hydrogen ion, H^+.

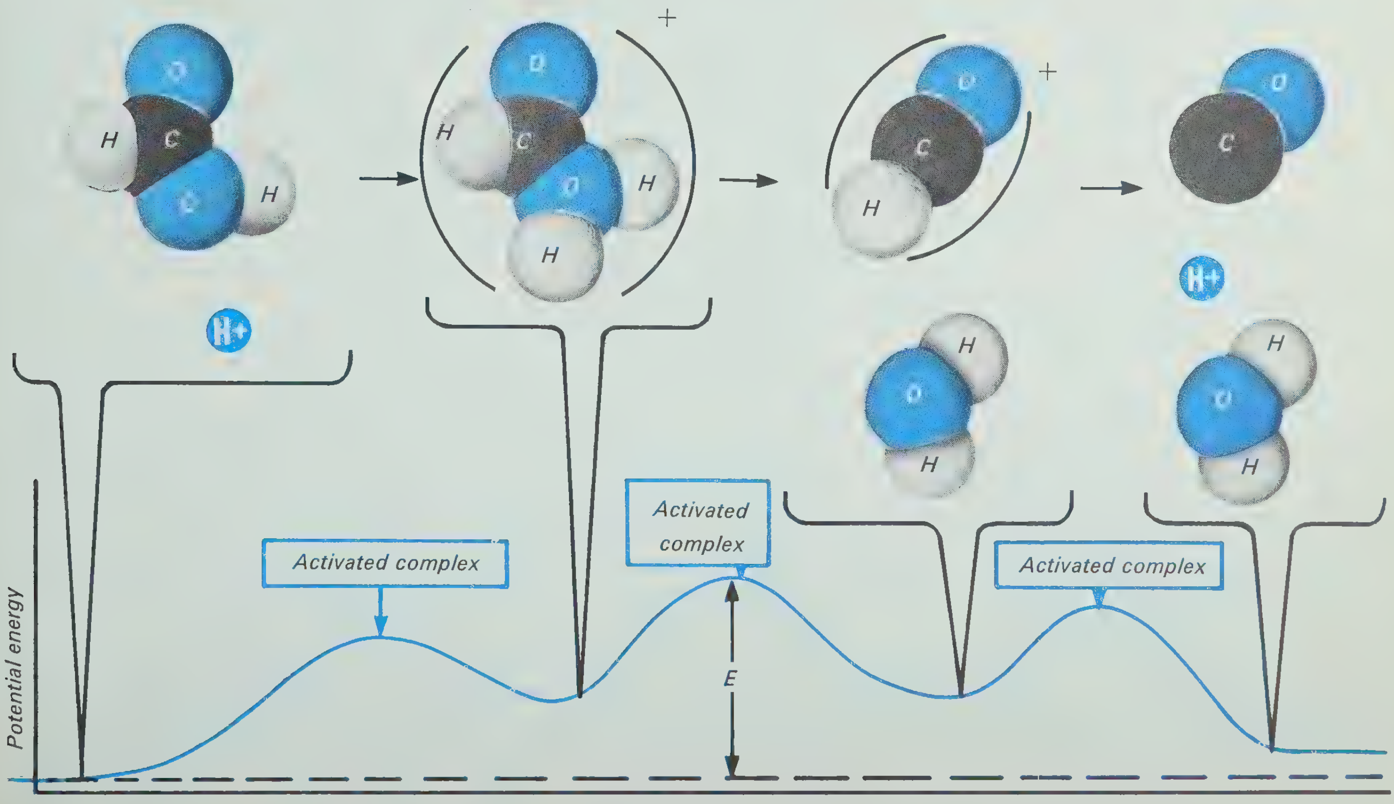
Consider now the decomposition of formic acid, HCOOH. This substance decomposes by two reaction paths. We will discuss the noncatalyzed path first. Figure 12-15 shows how this molecule might decompose. If the hydrogen atom attached to carbon migrates over to the OH group, the carbon-oxygen bond can break to give a molecule of water and a molecule of carbon monoxide. This migration, shown in the center drawing, requires a large amount of energy. This means there is a high activation energy. The reaction occurs very slowly.

$$HCOOH \longrightarrow CO + H_2O$$

If sulfuric acid, H_2SO_4, is added to an aqueous solution of formic acid, bubbles of carbon monoxide form rapidly. Catalysis also occurs if a different acid such as phosphoric acid, H_3PO_4, is used.

Chemists have a rather clear picture of how H^+ catalyzes the decomposition of HCOOH. The H^+ in the solution makes a new reaction path available. The new reaction mechanism begins with the addition of hydrogen ion to formic acid, as shown in Figure 12-16.

FIGURE 12-16 Mechanism and activation energy diagram for catalyzed decomposition of formic acid.



The catalyst is consumed first, forming the new species, $HCOOH_2^+$. In this species one of the carbon-oxygen bonds is weakened. With only a small expenditure of energy, the next reaction can occur, producing HCO^+ and H_2O. Finally, HCO^+ decomposes to produce carbon monoxide, CO, and H^+. This last reaction of the sequence regenerates the catalyst H^+.

$$\begin{array}{r}
HCOOH + H^+ \longrightarrow HCOOH_2^+ \\
HCOOH_2^+ \longrightarrow HCO^+ + H_2O \\
HCO^+ \longrightarrow CO + H^+ \\
\hline
HCOOH \longrightarrow CO + H_2O
\end{array}$$

Each of the steps in this new reaction mechanism is in agreement with the principles that apply to a simple reaction. Each reaction has an activation energy. The overall reaction has a potential energy diagram that is merely a composite of the energy curves for each reaction. Figure 12-16 shows the reaction and the composite potential energy diagram.

D. Other Catalysts

In some reactions, the catalyst is a solid substance on whose surface a reactant molecule can be held in a favorable position. The word **adsorption** is used to describe the interaction between the solid and the molecule. When a molecule of another reactant having enough energy reaches the same area on the solid, products form. Metals such as iron, nickel, and platinum act as catalysts for many reactions involving gases. There is some experimental evidence that the bonds in molecules held on the surface of solid catalysts are weakened or actually broken. The process of adsorption supplies energy to the molecular system. The bonds formed between the catalyst and the reactant release more energy than is required to break the bonds in the reactant. We can say that the adsorbed molecule exists in a high energy state. The second reactant molecule would not have to bring to the collision as much energy as in the noncatalyzed system. Many more collisions would provide the energy needed for reaction.

The substances called **enzymes** are important catalysts. There are many enzymes, found in living tissue, that have very specific catalytic functions. For example, ptyalin in saliva is important for the breakdown of the large starch molecules in our food. This process leads to much smaller molecules which can be utilized by body cells. Pepsin is another important enzyme. It serves as a catalyst for the conversion of proteins to simpler molecules. It is only in the past few years that chemists have been able to establish the molecular structure of some enzymes. It appears that the catalytic activity may reside in a rather small portion of the enzyme molecule.

Biochemistry is the branch of chemistry in which living plants and animals are studied. The application of chemical principles and an understanding of molecular structure have been important in many of the advances made in biochemistry. The rates of reactions and the catalysts that speed them up are particularly important.

12-9 Review

A simple and effective way of understanding the rates of chemical reactions is provided by the **collision theory.** The change from reactants to products requires a certain amount of energy, called a potential energy barrier. Colliding molecules must bring enough kinetic energy into a collision to achieve this energy. The minimum energy is called the **activation energy** and the molecular grouping temporarily formed is called the **activated complex.**

This theory shows that the rate of a reaction can be increased by *increasing the number of collisions per unit time* or by *increasing the kinetic energy brought to the collision.*

We can increase the number of collisions by raising the concentration or by raising the temperature.

We can increase the energy brought to the collision by raising the temperature.

A chemical reaction may proceed by a single step or it may occur by several successive steps. The detailed set of reactions is called the **reaction mechanism.** The rate of a chemical reaction is determined by the slowest or **rate-determining step** in the reaction mechanism.

Addition of a catalyst is another effective way to increase the rate of a chemical reaction. Catalysts alter the reaction mechanism and provide a second, lower energy path from reactants to products. Catalysts are regenerated at some point in the reaction mechanism. The search for catalysts for chemical reactions is an important area of chemical research. Although the function of a catalyst is understood in some systems, the mechanism is not yet understood in most reactions.

Questions and Problems for Chapter 12

1

The rate of movement of an automobile can be expressed in the units miles per hour. In what units would you discuss the rate of:

(a) movement of movie film through a projector;

(b) rotation of a motor shaft;

(c) gain of altitude;

(d) consumption of milk by a family;

(e) production of automobiles by an auto assembly plant.

2

Pick the member of each pair having the greater reaction rate. Assume similar conditions within each pair.

(a) Iron rusting or copper tarnishing.
(b) Wax burning or paper burning.
(c) Evaporation of gasoline or evaporation of water.

3

Explain (at the molecular level) why an increase in concentration of a reactant may cause an increase in rate of reaction.

4

The rate of a gaseous reaction may increase if the total pressure is increased. State three methods by which the pressure of a gaseous system might be increased.

5

Give two factors that would increase the rate of a reaction and explain why these do increase the rate.

6

Do you expect the equation

$$C_2H_4(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(g)$$

to represent the mechanism by which ethylene, C_2H_4, burns? Why?

7

A group of students is preparing a ten-page directory. The pages have been printed and are stacked in ten piles, page by page. The pages must be: (1) assembled in order, (2) straightened, and (3) stapled in sets. If three students work together, each performing a different operation, which might be the rate-controlling step? What would be the effect on the overall rate if the first step were changed by ten helpers joining the individual assembling the sheets? What if these ten helpers joined the student working on the second step? The third step?

8

Hydrogen peroxide reacts with iodide ion, according to this equation:

$$2\,H^+ + 2\,I^- + H_2O_2 \longrightarrow 2\,H_2O + I_2$$

The mechanism often suggested for this reaction is

$$H^+ + I^- + H_2O_2 \longrightarrow HOI + H_2O \qquad \text{slow}$$

$$H^+ + I^- + HOI \longrightarrow I_2 + H_2O \qquad \text{fast}$$

(a) Satisfy yourself that addition of these two equations gives the overall equation.
(b) How would you expect the rate to be affected if the I^- concentration is doubled?

9

Consider two gases *A* and *B* in a container at room temperature. What effect will the following changes have on the rate of the reaction between these gases?

(a) The pressure is doubled.
(b) The number of molecules of gas *A* is doubled.
(c) The temperature is decreased at constant volume.

10

In an important industrial process for producing ammonia (the Haber Process), the overall reaction is

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g) + 24{,}000 \text{ calories}$$

A yield of approximately 98% can be obtained at 200°C and 1000 atmospheres of pressure. The process makes use of a catalyst which is usually finely divided, mixed iron oxides containing small amounts of potassium oxide, K_2O, and aluminum oxide, Al_2O_3.

(a) Is this reaction exothermic or endothermic?
(b) Suggest a reason for the fact that this reaction is generally carried out at a temperature of 500°C and 350 atmospheres in spite of the fact that the yield under these circumstances is only about 30%.
(c) What is the ΔH for the reaction in kilocalories per mole of $NH_3(g)$?
(d) How many grams of hydrogen must react to form 1.60 moles of ammonia?

11

Describe the life and death of an ordinary, empty water glass. Utilize the concept "threshold energy."

12

Describe three situations at home or at school in which a minimum or threshold energy must be supplied before a "reaction" can take place.

13

Explain why food kept in a refrigerator does not spoil as rapidly as the same type of food left on the kitchen counter.

14

An increase in temperature of 10°C rarely doubles the kinetic energy of particles, and hence the number of collisions is not doubled. Yet, this temperature increase may be enough to double the rate of a slow reaction. How can this be explained?

15

In a collision of particles, what is the primary factor that determines whether a reaction will occur?

16

In Figure 12-11, why is kinetic energy decreasing as two HI go up the left side of the barrier and why is kinetic energy increasing as H_2 and I_2 go down the right side? Explain in terms of conservation of energy and also in terms of what is occurring to the various particles in relation to each other.

17

Phosphorus, P_4, exposed to air burns spontaneously to give P_4O_{10}; the ΔH of this reaction is -712 kcal per mole P_4.

(a) Draw an energy diagram for the net reaction, explaining the critical parts of the curve.
(b) How much heat is produced when 12.4 grams of phosphorus burn?

18

Considering that so little energy is required to convert graphite to diamond (recall Problem 14, Chapter 11), how do you account for the great difficulty found in the industrial process for accomplishing this?

19

Why does a burning match light a candle?

20

Draw an energy diagram for the reaction

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

(a) when the C is in large chunks of coal.
(b) Is the curve changed if very fine carbon powder is used?

21

Sketch a potential energy diagram which might represent an endothermic reaction. Label parts of curve representing activated complex, activation energy, net energy absorbed.

22

Draw potential energy diagrams for two reactions that have the same ΔH but one reaction is fast and the other is slow.

23

Why is it difficult to "hard-boil" an egg at the top of Pike's Peak? Is it also difficult to cook scrambled eggs there? Explain.

24

For the reaction $CO + NO_2 \longrightarrow CO_2 + NO$, the activation energy for the forward reaction is known to be $E_F = 32$ kcal/mole.

(a) Calculate ΔH for the reaction, using values from Table 11-2, p. 198.
(b) From E_F and ΔH, calculate E_R, the activation energy for the reverse reaction.
(c) Draw the potential energy diagram for this system, indicating E_F, E_R, and ΔH.

25

Explain why a catalyst increases the rates of chemical reactions the same amount for both the forward and reverse reactions.

26

The reaction of $S_2O_8^{2-}$ with I^- is catalyzed by Cu^{2+} ions. A suggested mechanism involves these steps.

$$2\,Cu^{2+} + 2\,I^- \xrightarrow{\text{fast}} 2\,Cu^+ + I_2$$

$$Cu^+ + S_2O_8^{2-} \xrightarrow{\text{slow}} CuSO_4^+ + SO_4^{2-}$$

$$Cu^+ + CuSO_4^+ \xrightarrow{\text{fast}} 2\,Cu^{2+} + SO_4^{2-}$$

Add these equations to show that Cu^{2+} is not consumed in the overall reaction.

27

Explain why there is danger of explosion where a large amount of dry, powdered, combustible material is produced.

28

For the reaction of marble, $CaCO_3(s)$, with acid,

$$CaCO_3(s) + 2\,H^+ \longrightarrow Ca^{2+} + CO_2(g) + H_2O,$$

compare the rate of reaction when $CaCO_3(s)$ is in the form of large marble chips or in the form of a fine dust.

29

Ra-226 is a radioactive isotope of radium with a half-life of 1600 years. If you wait 1600 years, half of the radium you started with has undergone radioactive decay. If you wait another 1600 years, you will have only one quarter of the radium you started with (one half of one half).

(a) Construct a graph of amount of Ra-226 as a function of time. Start with 1.0 gram of Ra-226 and show the amount after 1600, 3200, 4800, and 6400 years.

(b) Use your graph to estimate how much Ra-226 is present after one year, after ten years, and after 2400 years.

30

One gram of Ra-226 emits 3.7×10^{10} alpha particles per second. The nuclear reaction can be written

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

Calculate an approximate value for Avogadro's number. (In 1600 years, 0.5 gram of Ra-226 disappears. Compare the number of moles of Ra-226 with the total number of alpha particles given off in 1600 years.)

Equilibrium In Chemical Reactions

13

In the last chapter the rate of the reaction $2\ HI \longrightarrow H_2 + I_2$ was discussed. Then later in the chapter the rate of the reverse reaction $H_2 + I_2 \longrightarrow 2\ HI$ was considered. The rate of these gas phase reactions can be determined easily because iodine is the only colored substance present. In the first reaction, the purple color of iodine vapor becomes more intense as the reaction proceeds; in the second reaction, the color decreases in intensity as the reaction takes place. The discussion was limited to the initial phase of each reaction, where the amount of reaction was so small that the concentrations of the reactants could be considered constant.

In this chapter these and other reactions will be considered over longer periods of time. By direct observation of the color of iodine vapor, the $2\ HI \longrightarrow H_2 + I_2$ reaction can be followed. The I_2 concentration changes rapidly at first, but soon the color no longer changes. Figures 13-1 and 13-2 represent schematically what happens in each reaction. When observable changes no longer occur in the reacting chemical system, the system is in a **state of equilibrium.** The equilibrium situation raises many interesting questions. How is equilibrium recognized? What is the molecular behavior when a state of equilibrium is reached? What factors change the state of equilibrium? In this chapter we shall seek answers to these questions.

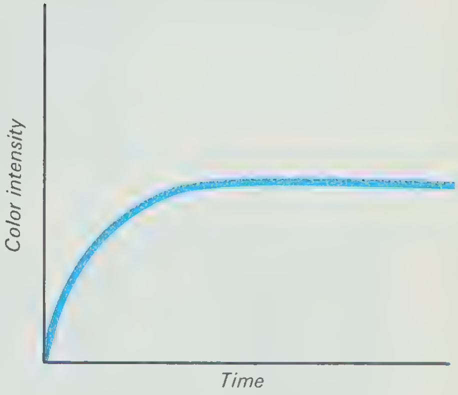


FIGURE 13-1

The change of color intensity for the reaction $2\ HI(g) \longrightarrow H_2(g) + I_2(g)$.

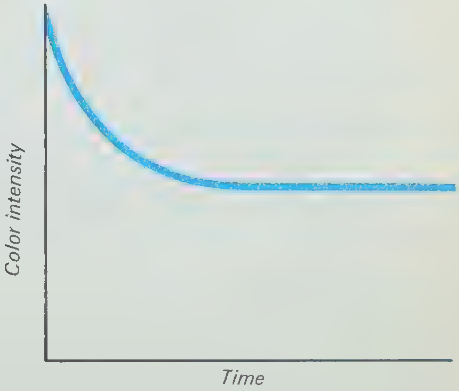


FIGURE 13-2

The change of color intensity for the reaction $H_2(g) + I_2(g) \longrightarrow 2\ HI(g)$.

QUALITATIVE ASPECTS OF EQUILIBRIUM

13-1 Recognizing Equilibrium

We have encountered equilibrium earlier in this course. When phase changes were discussed in Chapter 5, the liquid-gas equilibrium that fixes the vapor pressure of a liquid was considered. In Chapter 6, the solubility of a solid in a liquid was interpreted as an equilibrium situation. How is equilibrium recognized? Several experiments will help answer this question.

Experiment 1

When liquid water is placed in an evacuated flask at 25°C, the changes in gas pressure can be easily followed as some of the water evaporates. At first the pressure increases; but when it reaches 23.8 mm, the pressure remains constant as long as the temperature is constant. Since no further change in the system is observed, *the system is said to be at equilibrium.*

Experiment 2

If solid iodine is added to a water-alcohol mixture, a reddish color appears very quickly in the solution near the crystals. Iodine is dissolving. After a short while, no further change can be observed. The color of the solution stays constant, and the mass of the iodine crystals no longer changes as long as the temperature is constant. *The system has reached a state of equilibrium.* This experiment is shown in Figure 13-3.

Experiment 3

Fill two glass bulbs with nitrogen dioxide gas, at the same pressure. Place the first bulb in an ice bath and the second in boiling water. Figure 13-4 shows what is observed when equilibrium is established in each bulb. The gas in the bulb at 0°C is almost colorless. The gas in the second bulb, at 100°C, is reddish-brown. Other experiments show that most of the molecules in the colder bulb have the formula N_2O_4. Since the gas is almost colorless, N_2O_4 must not absorb visible light. On the other hand, experiments show that most of the molecules in the warmer bulb have the formula NO_2. Since the gas is reddish-brown in color, NO_2 must absorb visible light. When these bulbs are moved to a water bath at 25°C, the color of the gas changes. Figure 13-5 illustrates what happens. The color in bulb 1 deepens. A chemical change is occurring.

$$\text{bulb 1} \qquad \underset{\text{colorless}}{N_2O_4} \longrightarrow \underset{\text{reddish-brown}}{2\,NO_2}$$

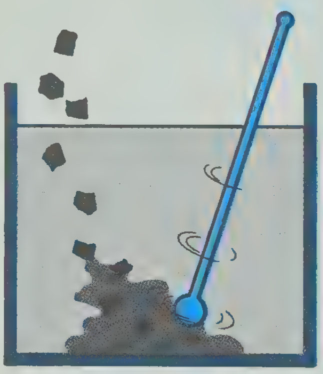
During the same time interval, the color in bulb 2 fades. A chemical change is taking place in this bulb also.

$$\text{bulb 2} \qquad \underset{\text{colorless}}{N_2O_4} \longleftarrow \underset{\text{reddish-brown}}{2\,NO_2}$$

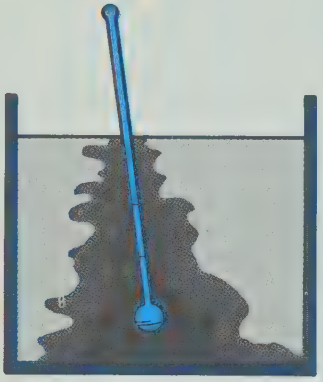
The gas color in the two bulbs becomes identical when they reach the same temperature. No further color changes occur. *A new state of equilibrium has been established in each bulb.*

What factors do these three experiments have in common? Are there similarities that help us recognize equilibrium? Yes, here is a list.

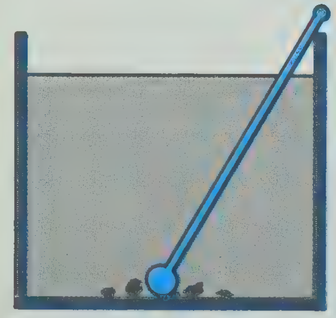
1. Equilibrium occurs only when a uniform temperature is maintained.
2. After the experiment was started, no substances were added to or taken from the system. Such a system is called a **closed system.**



Upon addition, solid I_2 begins to dissolve.



For a time it continues to dissolve.



Eventually, no further changes. Equilibrium exists.

FIGURE 13-3

Iodine dissolving in a stirred mixture of H_2O–alcohol. Equilibrium is recognized by constant color of the solution.

3. In each experiment, some easily measured property, such as pressure or color, changes with time and then reaches a constant value. There are no further changes in the system.

We can put these observations together in one generalization.

> *For a closed system at a uniform temperature, equilibrium is recognized by the constant properties of the system.*

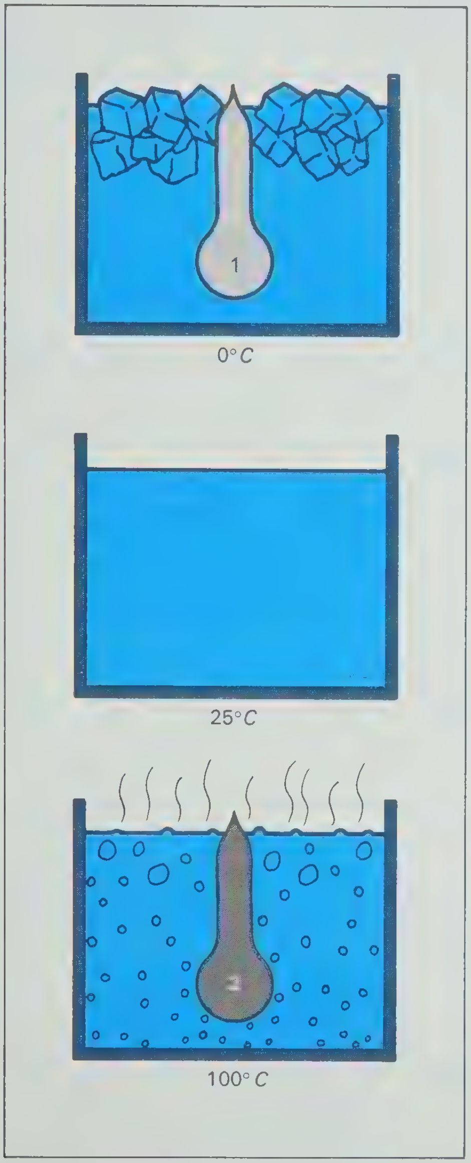


FIGURE 13-4

The equilibrium reaction $N_2O_4 \rightleftarrows 2\,NO_2$ at 0° and 100°C.

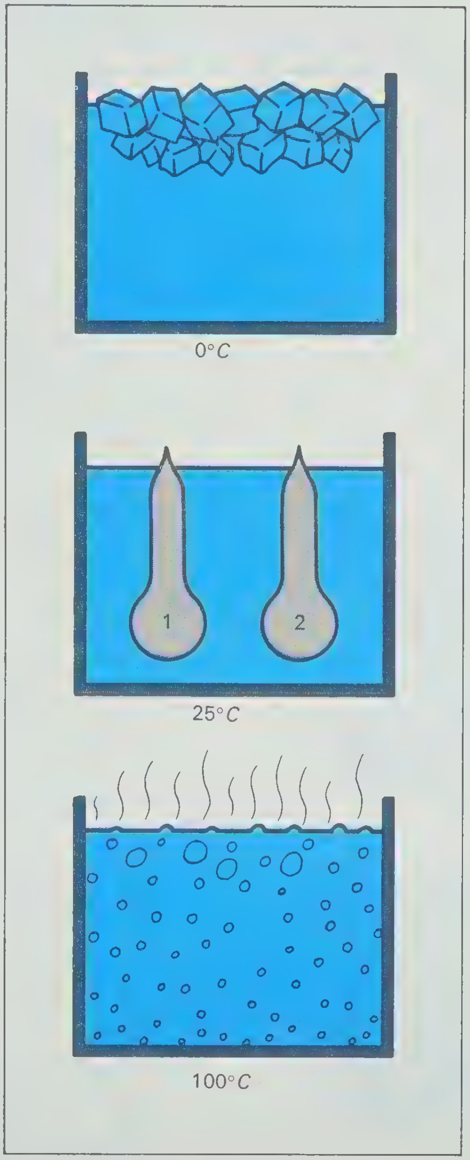


FIGURE 13-5

The equilibrium reaction $N_2O_4 \rightleftarrows 2\,NO_2$ at 25°C.

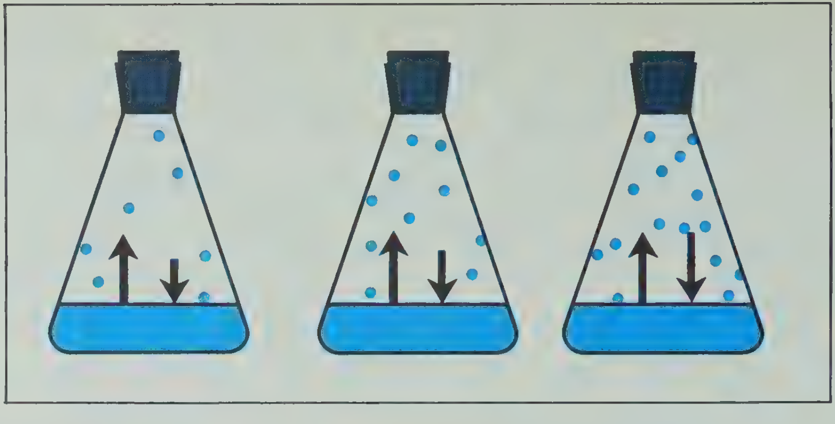


FIGURE 13-6

Equilibrium vapor pressure is a dynamic balance between evaporation and condensation.

13-2 The Dynamic Nature of Equilibrium

The Kinetic Theory led us to think of the evaporation of a liquid in terms of molecular behavior. Figure 13-6 shows schematically how equilibrium is established when water evaporates in a closed system. The size of each arrow indicates the rate at which molecules leave or return to the liquid. At first the gas pressure increases as the number of molecules in the gas phase increases. Soon the pressure reaches a constant value. The number of molecules entering the gas phase each second is the same as the number returning to the liquid. *Equilibrium is reached when there is a dynamic balance between evaporation and condensation.* At equilibrium, molecules continue to move back and forth between the two phases. Evaporation and condensation occur *at the same rate.*

The same explanation helps us understand how equilibrium is established when a crystal of iodine dissolves. Molecular vibration tends to dislodge a molecule from the surface of the crystal. The molecule is now free to move throughout the solvent. At first the rate at which molecules leave the crystal is much greater than the rate of their return. As the number of molecules in solution increases, the chance that a molecule will return to the crystal increases. This means that the rate at which molecules return to the crystal increases. Soon a balance between these rates is reached. Solubility equilibrium is established. Molecules leave the crystal and return to it *at the same rate.* Figure 13-7 shows schematically what takes place in solubility equilibrium.

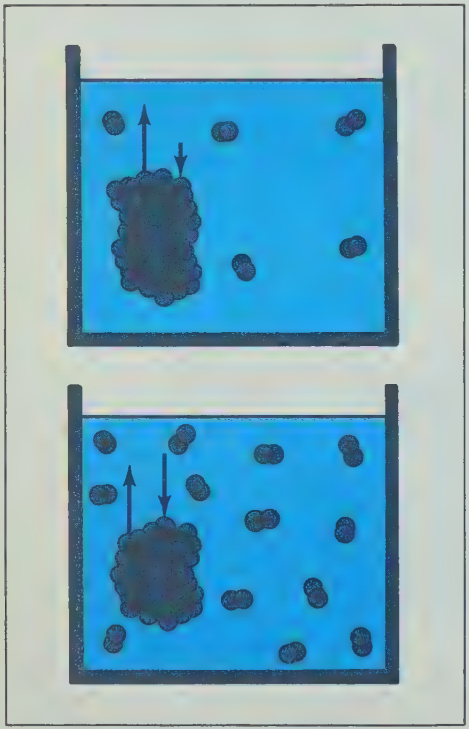


FIGURE 13-7

Equilibrium solubility is a dynamic balance between dissolving and crystallizing.

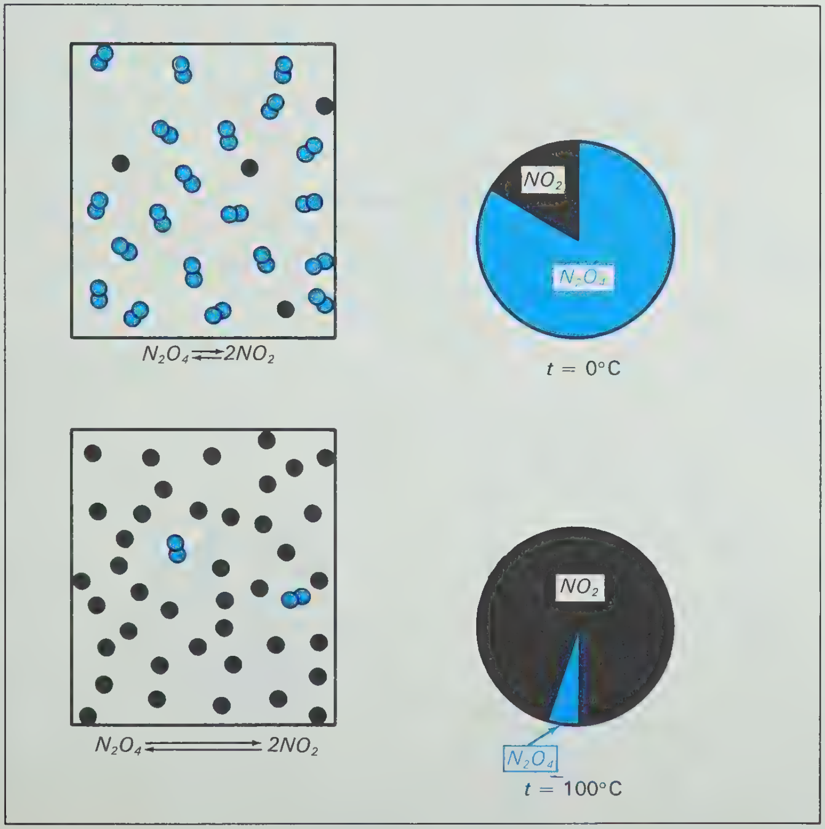
Now look at the N_2O_4–NO_2 system again. In Figure 13-8, a molecular view of the N_2O_4–NO_2 equilibrium is presented in schematic form. Each molecule of NO_2 is represented by a solid blue circle and each molecule of N_2O_4 is shown by two circles joined together. The color of the system at equilibrium is suggested by the drawing. The relative concentration for each gas is shown in the right-hand drawings where the labeled pieces are proportional to the number of molecules in the figure.

In the equations, arrows of equal length indicate that the system has reached a state of equilibrium. Throughout this discussion, the rate of a reaction will be indicated by the length of the arrow. At 0°C, short arrows emphasize that both rates of reaction are low. At 100°C, long arrows indicate that the rates of reaction are high. If both bulbs are transferred to a 25°C water bath, the reddish-brown color in bulb 1 becomes more intense. Chemical reaction is occurring to produce a higher concentration of NO_2. On the other hand, the color in bulb 2 fades rapidly. Chemical reaction takes place to produce a lower concentration of reddish-brown NO_2. How can these results be explained?

Raising the temperature increases the rate of a chemical reaction. Both the forward and the reverse reactions speed up when the temperature is changed from 0°C to 25°C. The fact that the color becomes more intense means that, initially, the rate of the forward reaction *is increased more* by the temperature change than is the rate of the reverse reaction.

$$\underset{\text{colorless}}{N_2O_4} \rightleftarrows \underset{\text{reddish-brown}}{2\,NO_2}$$

The net concentration of NO_2 increases. Now there will be more collisions between NO_2 molecules. This causes the rate of the reverse reaction to increase. Soon forward and reverse reaction rates are equal once more. The rates are greater than they were at 0°C. Equilibrium is established again.



$N_2O_4 \rightleftarrows 2NO_2$
NO_2
N_2O_4
t = 0°C
$N_2O_4 \rightleftarrows 2NO_2$
NO_2
N_2O_4
t = 100°C

FIGURE 13-8

The molecular view of the $N_2O_4 \rightleftarrows 2\,NO_2$ equilibrium at 0°C and 100°C.

What happens in bulb 2 when the temperature is lowered from 100°C to 25°C? Both the forward and the reverse reactions in bulb 2 slow down. The fact that the color becomes less intense must mean that the rate of the forward reaction *is decreased more* by the temperature change than is the rate of the reverse reaction.

$$\underset{\text{colorless}}{N_2O_4} \rightleftarrows \underset{\text{reddish-brown}}{2\,NO_2}$$

The net concentration of NO_2 *decreases.* As before, the rates of forward and reverse reactions soon become equal and a new state of equilibrium is reached. Figure 13-9 shows the situation in either bulb in the 25°C water bath.

These examples demonstrate that at the molecular level, equilibrium systems are dynamic, not static. Molecules interact continually, changing back and forth from one species to another. *The equality between the rates of the forward and reverse reactions gives the constant properties which we can observe and measure.*

ALTERING THE STATE OF EQUILIBRIUM

The concentration of NO_2 at equilibrium can be changed easily. Raising the temperature increases the NO_2 concentration. Lowering the temperature decreases the NO_2 concentration. What other factors might alter the relative concentrations of reactants and products at equilibrium? In the experiments discussed in Section 13-2, a state of equilibrium is reached when the rates of opposing reactions become equal. Therefore, any factor that changes the rate of one of the reactions involved in the equilibrium may affect the relative concentrations of reactants and products.

In Chapter 12 we saw that concentration, temperature, pressure, and the presence of a catalyst are factors that affect the rate of a reaction. Do these also affect the state of equilibrium? Additional examples will help us decide if there is a regularity.

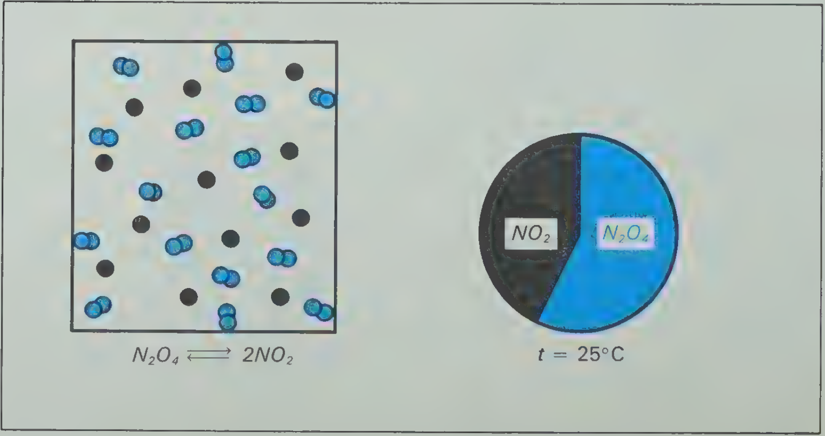


FIGURE 13-9

The molecular view of the $N_2O_4 \rightleftarrows 2\,NO_2$ equilibrium at 25°C.

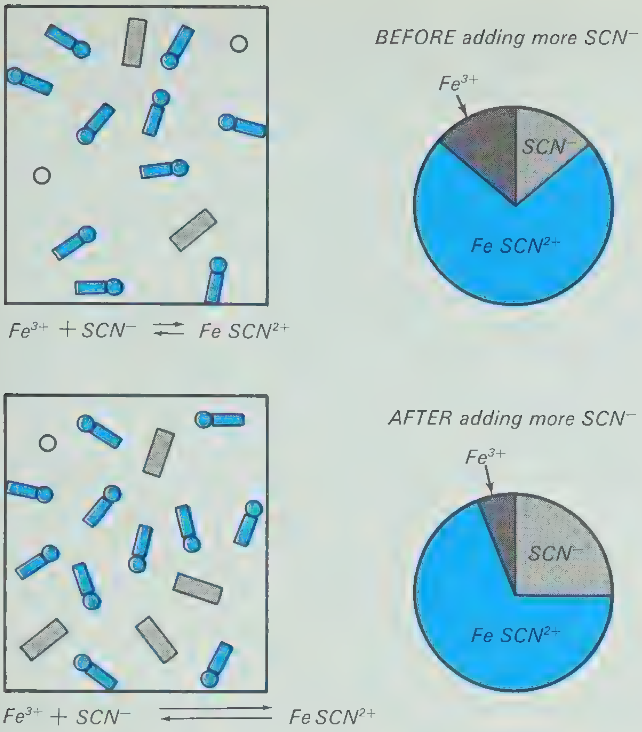

BEFORE adding more SCN^-
Fe^{3+}
SCN^-
$Fe\ SCN^{2+}$
$Fe^{3+} + SCN^- \rightleftharpoons Fe\ SCN^{2+}$
AFTER adding more SCN^-
Fe^{3+}
SCN^-
$Fe\ SCN^{2+}$
$Fe^{3+} + SCN^- \rightleftharpoons Fe\ SCN^{2+}$

FIGURE 13-10

The molecular view of the $Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$ equilibrium.

13-3 Effect of Concentration Changes

In Experiment 29, you studied the reaction between ferric ion and thiocyanate ion. The product of the reaction is an ion which has a deep red color. The equilibrium reaction is represented by the equation:

$$\underset{\text{light yellow}}{Fe^{3+}} + \underset{\text{colorless}}{SCN^-} \rightleftharpoons \underset{\text{deep red}}{FeSCN^{2+}}$$

Since the $FeSCN^{2+}$ ion is the only highly colored species in the system, the red color of the solution is a direct measure of its concentration. The color of the solution allows us to follow changes in the equilibrium state. What happens when crystals of NH_4SCN are added to the equilibrium system? The SCN^- concentration goes up as the crystals dissolve. Moreover, the red color of the solution deepens. The $FeSCN^{2+}$ concentration has increased too. *A new state of equilibrium is attained.*

In the original equilibrium, the rate of the reaction between Fe^{3+} and SCN^- is equal to the rate of dissociation of $FeSCN^{2+}$. When NH_4SCN crystals are added, the concentration of SCN^- increases. Because of this the number of collisions between Fe^{3+} and SCN^- goes up. The rate of the forward reaction increases. Then, as more $FeSCN^{2+}$ ions form, the rate of the reverse reaction increases too. A new state of equilibrium is achieved, with SCN^- and $FeSCN^{2+}$ concentrations higher than in the initial equilibrium. These changes can occur only if the Fe^{3+} concentration decreases. The schematic diagram in Figure 13-10 illustrates what happens. The arrows are longer in the second diagram, indicating that the rates of the reactions are larger than those represented in the first diagram. However, for each system *the rates are equal. Each system is at equilibrium.*

EXERCISE 13-1

Sodium chromate, Na_2CrO_4, dissolves in water to give a yellow solution. Sodium dichromate, $Na_2Cr_2O_7$, dissolves in water to give an orange solution. In either reaction, the equilibrium equation is

$$2\,CrO_4^{2-} + 2\,H^+ \rightleftarrows Cr_2O_7^{2-} + H_2O$$

a. What would happen if you added hydrochloric acid to a solution of sodium chromate?
b. What would happen if you added $Cr_2O_7^{2-}$ to the solution in part a?

13-4 Effect of Temperature Changes

It was shown in Section 13-2 that the concentrations of N_2O_4 and NO_2 at equilibrium are affected by temperature changes. Calorimetric measurements show that the decomposition of N_2O_4 is endothermic. We can include the heat energy in the equilibrium equation.

$$N_2O_4 + 14.1\text{ kcal} \rightleftarrows 2\,NO_2$$

When energy is added, the equilibrium system is subjected to a change. We observe that the reddish-brown color deepens. This color change means more NO_2 molecules form. Not all of the energy added to the system causes a temperature rise. Some of the energy is absorbed by N_2O_4 molecules. Some of the energy breaks chemical bonds instead of raising the temperature.

EXERCISE 13-2

How would the addition of more energy affect the amount of NH_3 at equilibrium in this reaction?

$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g) + 22\text{ kcal}$$

13-5 Effect of Pressure Changes

In Section 13-3 the effect of changing the concentration of one component in an equilibrium system was discussed. What would happen if the concentrations of all components were altered? This can most easily be done with a gas phase equilibrium by changing the volume of the system. The N_2O_4–NO_2 equilibrium can be our example.

$$N_2O_4(g) \rightleftarrows 2\,NO_2(g)$$

A sudden decrease in volume by a factor of two doubles the partial pressure of each gas. We might expect the color of the gases to deepen because the molecules are crowded closer together. When this experiment is carried out, the gas is darker in color for a moment. But then the reddish-brown color of NO_2 diminishes somewhat and becomes constant. At equilibrium, the system is *lighter* in color than it was immediately after the pressure increase. This reduction in color means that the concentration of NO_2 has decreased. The balanced equation tells us that two moles of NO_2 must react to form one mole of N_2O_4. There are fewer molecules per liter, producing less gas pressure. The total pressure in the system decreases as N_2O_4 forms. We tried to raise the pressure by decreasing the volume. Chemical reaction occurred in the system so that the total number of molecules decreased. At equilibrium the pressure is then not quite as large as the volume change alone would have made it. Neither is the color as dark as that produced by the initial pressure increase.

A change in pressure does not always affect an equilibrium state. Look at the H_2–I_2–HI equilibrium once more.

$$H_2 + I_2 \rightleftarrows 2\,HI$$

Decreasing the volume increases the partial pressure of each gas. However, the moles of I_2 do not change. The total pressure is not relieved by chemical change whether reactants form more products or products form more reactants. The total number of molecules stays the same during chemical change in this system.

EXERCISE 13-3

What happens in these gas phase equilibria if the volume of each system is increased by a factor of two?

$$PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g)$$
$$2\,NO(g) \rightleftarrows N_2(g) + O_2(g)$$
$$4\,NH_3(g) + 5\,O_2(g) \rightleftarrows 4\,NO(g) + 6\,H_2O(g)$$

13-6 Effect of a Catalyst on Equilibrium

You have seen in your laboratory work that Cu^{2+} functions as a catalyst, increasing the rate of reaction between I^- and $S_2O_8{}^{2-}$. In Section 12-8, other examples of catalysis were discussed. Chemists have found in many different experiments that addition of a catalyst has no effect on the equilibrium concentrations of reactants or products. At first this may be surprising. However, if you had determined product concentrations in the I^-–$S_2O_8{}^{2-}$ reaction, with and without a catalyst, you would have found the equilibrium states were the same. Why is this? Look back at Figure 12-8, page 215, which shows the activation energy diagram for a catalyzed reaction. A catalyst speeds up a reaction by providing a low-energy reaction path from reactants to products. At the same time this low-energy path becomes available for the reverse reaction. Both the forward and the reverse reaction rates increase by the same amount. Because of this situation, *a catalyst produces no net change in the equilibrium system.* The system reaches equilibrium much more rapidly when a catalyst is present, but the equilibrium concentrations of reactants and products are not changed.

13-7 Le Chatelier's Principle: A Regularity

We have seen that equilibrium is attained in a chemical system when the rates of opposing reactions become equal. Anything that changes the rate of either reaction in the equilibrium system may affect the equilibrium concentrations. A regularity first proposed by a French chemist, Henry Louis Le Chatelier, helps us to predict whether the concentrations of reactants or products are favored by some change.

Le Chatelier studied the effects in a large number of chemical equilibria when temperature, pressure, or concentration were altered. The regularity that he proposed can be stated this way:

> *If a closed system at equilibrium is subjected to a change, processes occur that tend to counteract that change.*

This generalization has been found to be applicable to such a large number of systems that it is now called **Le Chatelier's Principle.** Table 13-1 summarizes the different systems we have discussed.

TABLE 13-1

An Important Regularity, Le Chatelier's Principle

Reaction	Change	Reaction Behavior	Final Result
$Fe^{3+} + SCN^- \rightleftarrows FeSCN^{2+}$	Add SCN^-.	The concentration of $FeSCN^{2+}$ increases, using up some Fe^{3+} and some SCN^-.	New equilibrium concentration for SCN^- is lower than the sum of added plus original concentration.
$N_2O_4 + 14.1\text{ kcal} \rightleftarrows 2\ NO_2$	Add heat energy.	Color of gas darkens. Some N_2O_4 decomposes to NO_2, absorbing energy.	New equilibrium temperature is lower than expected.
$N_2O_4(g) \rightleftarrows 2\ NO_2(g)$	Increase pressure by reducing volume.	Color of gas darkens then fades slightly. Some NO_2 forms N_2O_4. Total number of molecules decreases.	New equilibrium pressure is lower than expected from the volume change.
$H_2(g) + I_2(g) \rightleftarrows 2\ HI(g)$	Increase pressure by reducing volume.	Both rates increase equally. Total number of molecules is constant.	New equilibrium pressure is the pressure expected for the volume change.
Any reaction at equilibrium	Add catalyst.	Equilibrium state remains the same but is reached more rapidly.	A catalyst does not affect equilibrium concentrations.

13-8 The Synthesis of Ammonia by the Haber Process

The principles we have been discussing can be applied to some large-scale industrial processes. **Fixed nitrogen** is nitrogen in chemical compounds rather than nitrogen that is in the form of the element, N_2. There is an almost inexhaustible supply of N_2 in the atmosphere. However, N_2 has very low chemical activity.

In 1898 nearly two thirds of the world's supply of fixed nitrogen came from nitrate deposits in Chile. Huge as the Chilean nitrate deposits were, scientists predicted that the world's requirement of nitrogen compounds for fertilizers and for explosives would soon exceed the supply. It was essential that an economical method be developed to convert atmospheric nitrogen into a compound such as NH_3 or NO_2. Fritz Haber, a German scientist, successfully developed a process by which atmospheric nitrogen is converted into ammonia.

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3 + 22\text{ kcal}$$

Can we predict the best conditions for a high yield of ammonia?

The formation of NH_3 represents a decrease in total moles of gas from 4 moles to 2 moles. Therefore, we know from Le Chatelier's Principle that high pressure would increase the relative amount of NH_3 at equilibrium. The reaction to form NH_3 is exothermic. From Le Chatelier's Principle we can readily see that a high temperature favors the decomposition of NH_3. Low temperature favors formation of NH_3.

But are these conditions practical? Reaction rates are low at low temperatures. A compromise is needed. Low temperature favors NH_3 formation. High temperature is necessary for a satisfactory reaction rate. The compromise used for the industrial process involves an intermediate temperature near 500°C. Even then the success of the process depends upon the presence of a suitable catalyst to achieve a reasonable reaction rate.

Another compromise is needed in deciding on the pressure conditions. It is expensive to build high-pressure equipment. A pressure of about 350 atmospheres is used. Yet with these conditions, 350 atmospheres and 500°C, only about 30% of the reactants are converted to NH_3. Ammonia is removed from the mixture by liquefying it under conditions at which N_2 and H_2 remain gases. The unreacted N_2 and H_2 are then recycled until the conversion to NH_3 is very high.

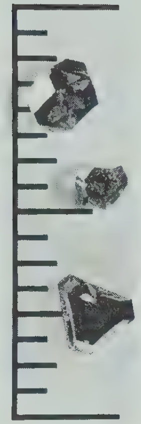
Almost all of the nitrogen compounds that are used today are derived from NH_3 made by the Haber Process.

13-9 Production of Diamonds from Graphite

World diamond production, 1965
5 Tons mined
0.5 Ton man-made

Chemists have recognized since 1880 the conditions needed to convert graphite to diamond. In 1955 this conversion was accomplished. Now synthetic diamonds are made for industrial use. The equilibrium that we must consider can be written

$$\text{C (graphite)} + 0.45 \text{ kcal} \rightleftarrows \text{C (diamond)}$$


1 inch

Synthetic diamonds about 1 carat

The density of diamond is greater than the density of graphite. This means the molar volume of diamond is less than the molar volume of graphite. Therefore, high pressure would favor formation of diamond. Since the reaction is endothermic, high temperature would increase the amount of diamond produced. At the present stage of development, the commercial production of diamond requires temperatures near 2000°C and pressures in the range of 50,000 to 100,000 atmospheres. Even at these conditions catalysts are needed to obtain a useful rate. Metals such as chromium, iron, and platinum serve as catalysts. Although diamonds formed by this process are not gemlike in appearance, they are very valuable. Because of their hardness, these synthetic diamonds are widely used in cutting and grinding operations.

QUANTITATIVE ASPECTS OF EQUILIBRIUM

13-10 The Equilibrium Constant

In the laboratory you studied the reaction

$$Fe^{3+} + SCN^- \rightleftarrows FeSCN^{2+}$$

From the red color of the solution you estimated the concentration of $FeSCN^{2+}$. We will use square brackets to mean concentration. For example, **[$FeSCN^{2+}$]** is the chemist's shorthand way of saying "the concentration of $FeSCN^{2+}$ in moles per liter." After calculating values for $[Fe^{3+}]$ and $[SCN^-]$, you combined these three concentration terms in various ways and found that the ratio

$$\frac{[FeSCN^{2+}]}{[Fe^{3+}] \times [SCN^-]}$$

was approximately constant. Look back at the equilibrium reaction. You can see that the concentration of the *product*, $FeSCN^{2+}$, appears in the numerator. The concentrations of the *reactants* are multiplied, $[Fe^{3+}] \times [SCN^-]$, and are placed in the denominator. Arranging the concentrations this way gives a constant. Even though the concentrations of these species may vary a great deal, this ratio does not vary appreciably as long as the temperature is held constant. You may have wondered why the reciprocal of the ratio was not used. It too gives a constant. The decision was a matter of choice. Chemists have agreed to use the ratio with concentrations of products in the numerator and with concentrations of reactants in the denominator.

Accurate data on the H_2–I_2–HI system at equilibrium is shown in Table 13-2. Concentration units are moles per liter. These data can be used to calculate values for various combinations of concentrations found at equilibrium in the system

$$2\,HI(g) \rightleftarrows H_2(g) + I_2(g)$$

The results are shown in Table 13-3. One combination of terms does not give constant values. The other set gives very good results.

TABLE 13-2

Equilibrium Concentrations for
HI, H_2, and I_2 at 700°K

Experiment Number	$[HI]$	$[H_2]$	$[I_2]$
1	17.7×10^{-3}	1.83×10^{-3}	3.13×10^{-3}
2	16.5×10^{-3}	2.91×10^{-3}	1.71×10^{-3}
3	13.5×10^{-3}	4.56×10^{-3}	0.74×10^{-3}
4	3.53×10^{-3}	0.48×10^{-3}	0.48×10^{-3}
5	8.41×10^{-3}	1.14×10^{-3}	1.14×10^{-3}

Values in experiments 1, 2, 3 were obtained by heating H_2 and I_2. Values in experiments 4 and 5 were obtained by heating HI.

TABLE 13-3

Values for Various Ratios for
Data in Table 13-2

Experiment Number	$\frac{[H_2][I_2]}{[HI]}$	$\frac{[H_2][I_2]}{[HI]^2}$
1	3.24×10^{-4}	1.83×10^{-2}
2	3.02×10^{-4}	1.83×10^{-2}
3	2.50×10^{-4}	1.85×10^{-2}
4	0.65×10^{-4}	1.85×10^{-2}
5	1.55×10^{-4}	1.84×10^{-2}
	Ratio Not Constant	Ratio Constant

We can write

$$\frac{[H_2][I_2]}{[HI]^2} = \text{a constant} = 1.84 \times 10^{-2} \text{ (at 700°K)}$$

This ratio is the product of the equilibrium concentrations of hydrogen and iodine, the substances produced in the reaction

$$[H_2] \times [I_2]$$

divided by the square of the concentration of the reacting substance

$$[HI]^2$$

In this ratio, the power to which we raise the concentration of each substance is equal to its coefficient in the balanced chemical equation. Perhaps this may be clearer to you if we wrote the chemical equation in a slightly different way.

$$HI + HI \rightleftarrows H_2 + I_2$$

Then our constant ratio has the form

$$\frac{[H_2][I_2]}{[HI][HI]} = \frac{[H_2][I_2]}{[HI]^2}$$

13-11 The Law of Chemical Equilibrium

These observations and many others like them lead to the generalization known as the **Law of Chemical Equilibrium.** Consider the reaction

$$aA + bB \rightleftarrows eE + fF$$

When equilibrium is established, a simple relation always exists between the concentrations of products, $[E]$ and $[F]$, and the concentrations of reactants, $[A]$ and $[B]$.

$$\frac{[E]^e\ [F]^f}{[A]^a\ [B]^b} = K = \text{a constant}$$

Some more examples may help. Table 13-4 lists some chemical reactions. The equilibrium law expression is given for each reaction.

TABLE 13-4

Some Equilibrium Constants

Reaction	Equilibrium Law Expression	K, at Stated Temperature
$Ag^+ + 2\,NH_3 \rightleftarrows Ag(NH_3)_2{}^+$	$K = \frac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$	1.7×10^7 at 25°C
$N_2O_4(g) \rightleftarrows 2\,NO_2(g)$	$K = \frac{[NO_2]^2}{[N_2O_4]}$	8.3×10^{-1} at 55°C
$2\,HI(g) \rightleftarrows H_2(g) + I_2(g)$	$K = \frac{[H_2][I_2]}{[HI]^2}$	1.84×10^{-2} at 423°C
$HSO_4{}^- \rightleftarrows H^+ + SO_4{}^{2-}$	$K = \frac{[H^+][SO_4{}^{2-}]}{[HSO_4{}^-]}$	1.3×10^{-2} at 25°C
$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$	$K = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$	1.8×10^{-5} at 25°C

There are several points in this table that should be emphasized. First, K may be a large number. It may be a small number. Only through experiments can we know the numerical value for K. Second, each substance must be present at equilibrium. If this condition were not satisfied, one of the concentration terms in the expression for the equilibrium constant would be equal to zero. K may be small, but it is never equal to zero.

What does the numerical value for K tell us? If K is large, either the numerator in the equilibrium expression must be large or the denominator must be small. Either way, at equilibrium there is a high concentration of products relative to reactants. A small value for K means the opposite. At equilibrium there is a high concentration of reactants relative to products. Whenever you see a numerical value for an equilibrium constant, K, think of it this way:

> A large value for K means products are favored.
> A small value for K means reactants are favored.

For the reaction

$$H_2O \rightleftharpoons H^+ + OH^-$$

the equilibrium expression would be written

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

The very low conductivity of water provides evidence that only a small fraction of the water molecules form ions. Thus the concentration of water has essentially a constant value fixed by its density and molar mass. It is convenient to combine K and $[H_2O]$ to define a new constant, K_w.

$$K_w = [H^+][OH^-] = K \times [H_2O]$$

Convince yourself that the concentration of water is approximately constant by completing Exercise 13-4.

EXERCISE 13-4

a. Water has a density of one gram per milliliter. Calculate the concentration of water in moles per liter in pure water.
b. Now calculate the concentration of water in 0.10 M aqueous solution of acetic acid, CH_3COOH, assuming each molecule of CH_3COOH occupies the same volume as one molecule of H_2O.

The same kind of argument applies to the reaction

$$Cu(s) + 2\,Ag^+ \rightleftharpoons 2\,Ag(s) + Cu^{2+}$$

Chemists have found it convenient to write the equilibrium law expression this way

$$K = \frac{[Cu^{2+}]}{[Ag^+]^2}$$

You might have expected the expression

$$K' = \frac{[Cu^{2+}][Ag]^2}{[Cu][Ag^+]^2}$$

The concentration terms for solid Cu and solid Ag are combined with the equilibrium constant K' somewhat as the concentration of H_2O "disappeared" in the previous example. The concentration of a solid is fixed by its density. As long as the temperature and pressure are kept constant, the concentration of a solid does not change.

Whenever an equilibrium system includes water or a solid like Cu or Ag, concentration terms for these substances do not appear in the equilibrium law expression. Some additional examples are given in Table 13-5.

TABLE 13-5

More Equilibrium Constants

Reaction	Equilibrium Expression	K at 25°C
$Cu(s) + 2\,Ag^+ \rightleftarrows 2\,Ag(s) + Cu^{2+}$	$K = \frac{[Cu^{2+}]}{[Ag^+]^2}$	2×10^{15}
$Cu(s) + Cu^{2+} \rightleftarrows 2\,Cu^+$	$K = \frac{[Cu^+]^2}{[Cu^{2+}]}$	1×10^{-6}
$AgCl(s) \rightleftarrows Ag^+ + Cl^-$	$K_{sp} = [Ag^+][Cl^-]$	1.7×10^{-10}
$H_2O \rightleftarrows H^+ + OH^-$	$K_w = [H^+][OH^-]$	1.0×10^{-14}
$AgI(s) \rightleftarrows Ag^+ + I^-$	$K_{sp} = [Ag^+][I^-]$	8.5×10^{-17}

EQUILIBRIUM CALCULATIONS

13-12 The Solubility Product, K_{sp}

When silver chloride dissolves in water, silver ions, Ag^+, and chloride ions, Cl^-, are found in the solution in equilibrium with the solid AgCl. The concentrations of these species, Ag^+ and Cl^-, are the ones which fix the equilibrium solubility. The equilibrium equation which represents AgCl dissolving in water is

$$AgCl(s) \rightleftarrows Ag^+ + Cl^-$$

The equilibrium expression has the form

$$K_{sp} = [Ag^+][Cl^-]$$

For lead chloride, $PbCl_2$, we write

$$PbCl_2(s) \rightleftharpoons Pb^{2+} + 2\,Cl^-$$
$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

Solubility equilibrium expressions are given a special name, the **solubility product.** The symbol K_{sp} is used. A low value of K_{sp} means the concentrations of ions are low, at equilibrium. Consequently, a low value for K_{sp} must mean that the solubility is very low. Some K_{sp} values are given in Table 13-6.

TABLE 13-6

Some Solubility Products at 25°C

Compound	K_{sp}	Compound	K_{sp}
AgCl	1.7×10^{-10}	$SrCrO_4$	3.6×10^{-5}
AgBr	5.0×10^{-13}	$BaCrO_4$	8.5×10^{-11}
AgI	8.5×10^{-17}	$PbCrO_4$	2×10^{-16}
$AgBrO_3$	5.4×10^{-5}		
$AgIO_3$	3.1×10^{-8}	$CaSO_4$	2.4×10^{-5}
		$SrSO_4$	7.6×10^{-7}
		$PbSO_4$	1.3×10^{-8}
		$BaSO_4$	1.5×10^{-9}
		$RaSO_4$	4×10^{-11}

EXERCISE 13-5

Write the equation for the dissolving of calcium sulfate, $CaSO_4$. Write the solubility product expression.

EXERCISE 13-6

Write the equation for the dissolving of silver chromate, Ag_2CrO_4. Write the solubility product expression. Silver chromate dissolves to give Ag^+ and CrO_4^{2-} ions.

EXERCISE 13-7

Compare the K_{sp} values for AgCl, AgBr, and AgI. Which of these compounds is most soluble in water? Which is least soluble?

13-13 Calculation of the Solubility of Silver Chloride in Water

Suppose we wish to know how much AgCl will dissolve in one liter of water at 25°C. Find the numerical value of K_{sp} in Table 13-6.

$$K_{sp} = [Ag^+][Cl^-] = 1.7 \times 10^{-10}$$

Silver chloride dissolves until the concentration of silver ions and chloride ions increases enough to make their product equal to 1.7×10^{-10}.

We can designate the solubility of AgCl in water by the symbol, s. This symbol, s, equals the number of moles of solid AgCl that dissolve to make one liter of saturated solution. If s moles of AgCl dissolve, s moles of Ag^+ and s moles of Cl^- are produced in one liter.

$$[Ag^+] = [Cl^-] = s \text{ moles/liter}$$

Substituting into the K_{sp} expression we can calculate the value for s, the solubility of AgCl.

$$\begin{aligned} K_{sp} &= [Ag^+][Cl^-] = s \times s \\ K_{sp} &= s^2 = 1.7 \times 10^{-10} \\ s &= \sqrt{1.7 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ mole/liter} \end{aligned}$$

AgCl is not very soluble. Only 0.000013 mole of AgCl is contained in one liter of its saturated solution at 25°C.

EXERCISE 13-8

Calculate the solubility, in moles per liter, of calcium sulfate in water, using the solubility product given in Table 13-6.

13-14 Will a Precipitate Form?

When two solutions are mixed, a precipitate may form. For example, suppose solutions of calcium chloride, $CaCl_2$, and sodium sulfate, Na_2SO_4, are mixed. The mixture contains both calcium ions, Ca^{2+}, and sulfate ions, $SO_4{}^{2-}$. The solubility product permits us to predict whether solid calcium sulfate will form. Consider two examples to show how the prediction is made:

Example 1. Equal volumes of 0.02 *M* $CaCl_2$ and 0.0004 *M* Na_2SO_4 are mixed.

Example 2. Equal volumes of 0.08 *M* $CaCl_2$ and 0.02 *M* Na_2SO_4 are mixed. Will a precipitate form in either example?

First we must write the balanced equation for the reaction of calcium sulfate dissolving in water and then use the equilibrium expression:

$$CaSO_4(s) \rightleftarrows Ca^{2+} + SO_4{}^{2-}$$
$$K_{sp} = [Ca^{2+}][SO_4{}^{2-}]$$

The next step is to find the concentration of each ion in the final mixture. After equal volumes of each solution are mixed, each ion is present in twice as much solution. The final ionic concentration is only half as great as before mixing.

Example 1. $$[\mathrm{Ca}^{2+}] = \frac{0.02\ M}{2} = 0.01\ M = 1 \times 10^{-2} M$$

$$[\mathrm{SO}_4^{\ 2-}] = \frac{0.0004\ M}{2} = 0.0002\ M = 2 \times 10^{-4}\ M$$

A trial value of the ion product must be compared to K_{sp}.

$$\begin{aligned}[\mathrm{Ca}^{2+}] \times [\mathrm{SO}_4^{\ 2-}] &= (1 \times 10^{-2}) \times (2 \times 10^{-4}) \\ &= 2 \times 10^{-6}\end{aligned}$$

The trial product, 2×10^{-6}, is less than K_{sp}, 2.4×10^{-5}. *Precipitation will not occur in Example 1.*

Example 2. $$[\mathrm{Ca}^{2+}] = \frac{0.08\ M}{2} = 0.04\ M = 4 \times 10^{-2}\ M$$

$$[\mathrm{SO}_4^{\ 2-}] = \frac{0.02\ M}{2} = 0.01\ M = 1 \times 10^{-2}\ M$$

Again we calculate the trial value of the ion product.

$$\begin{aligned}[\mathrm{Ca}^{2+}] \times [\mathrm{SO}_4^{\ 2-}] &= (4 \times 10^{-2}) \times (1 \times 10^{-2}) \\ &= 4 \times 10^{-4}\end{aligned}$$

This time the trial product, 4×10^{-4}, is greater than K_{sp}, 2.4×10^{-5}. *A precipitate will form.* Solid $CaSO_4$ will continue to form until values of $[\mathrm{Ca}^{2+}]$ and $[\mathrm{SO}_4^{\ 2-}]$ become low enough that the ion product equals K_{sp}. Then equilibrium exists and the rate of dissolving equals the rate of precipitation.

EXERCISE 13-9

A 50 ml volume of 0.04 M $Ca(NO_3)_2$ solution is added to 150 ml of 0.008 M $(NH_4)_2SO_4$ solution. Show that a trial value of the ion product for calcium sulfate is 6×10^{-5}. Will a precipitate form?

13-15 The Factors Which Determine Equilibrium

Why does one reaction favor reactants and another reaction favor products? What factors cause sodium chloride to have a large solubility in water and silver chloride to have a low solubility? Why does equilibrium favor the reaction of oxygen with iron to form Fe_2O_3 but not the reaction of oxygen with gold? As scientists, we cannot help wondering what factors determine the conditions at equilibrium.

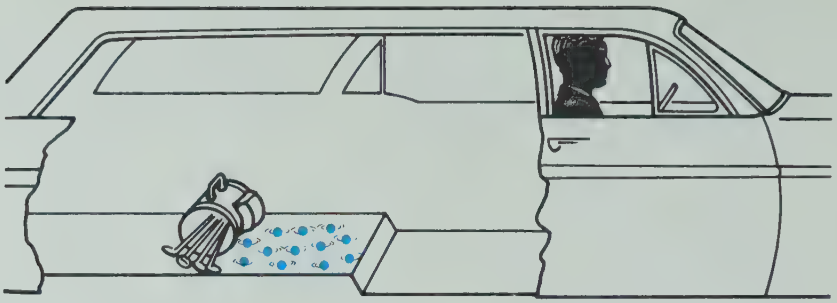


FIGURE 13-11

Golf balls rolling on the floor of a station wagon.

This is the activity of science we called "wondering why." Perhaps looking at a familiar situation will help us find an explanation. Figure 13-11 shows a station wagon being driven down a smooth road. A golf bag has been thrown into the rear of the station wagon. Unfortunately, the ball pocket is open. All of the golf balls have spilled out onto the floor of the station wagon. Because the floor has a step in it, the golf balls on the upper level possess some potential energy. The golf balls tend to roll to the lower level spontaneously. As each golf ball does this, its potential energy becomes kinetic energy. Finally, the kinetic energy is dissipated as heat energy in the floor of the station wagon. Now the golf balls lie at rest at the lower floor level.

This situation is similar to the chemical change in a spontaneous, exothermic reaction. The reactants, with high heat content, react spontaneously to form products, with lower heat content. As each molecular reaction occurs, the excess heat content becomes kinetic energy. As the product molecules collide with other molecules, this energy is dissipated in the form of heat energy. The comparison of a chemical reaction to golf balls rolling downhill is illustrated in Figure 13-12.

Let's list the similarities.

(1) There are two states of each system.

	Initial State		*Final State*
Golf balls:	on upper level	⟶	on lower level
Reaction:	reactants	⟶	products

(2) The potential energy of the initial state is higher than the potential energy of the final state.

	Initial State		*Final State*
Golf balls:	high potential energy	⟶	low potential energy
Reaction:	high heat content	⟶	low heat content

(3) As the change from initial state to final state proceeds, the form of the energy changes.

	Initial State		*Final State*
Golf balls:	potential energy	→	kinetic energy, and then heat
Reaction:	heat content	→	molecular kinetic energy, and then heat

(4) The changes from initial to final state proceed spontaneously toward lowest potential energy. Both systems "roll down" an energy hill.

	Initial State	→	*Final State*
Golf balls:		spontaneous	
Reaction:		spontaneous	

Is there a useful "regularity" that we can see here? Golf balls always roll downhill spontaneously. Perhaps chemical reactions always move spontaneously in the direction of minimum energy.

This proposal leads us to expect that a reaction will take place if the products have lower heat content than the reactants. We usually find this to be true, especially for reactions which release a large amount of heat.

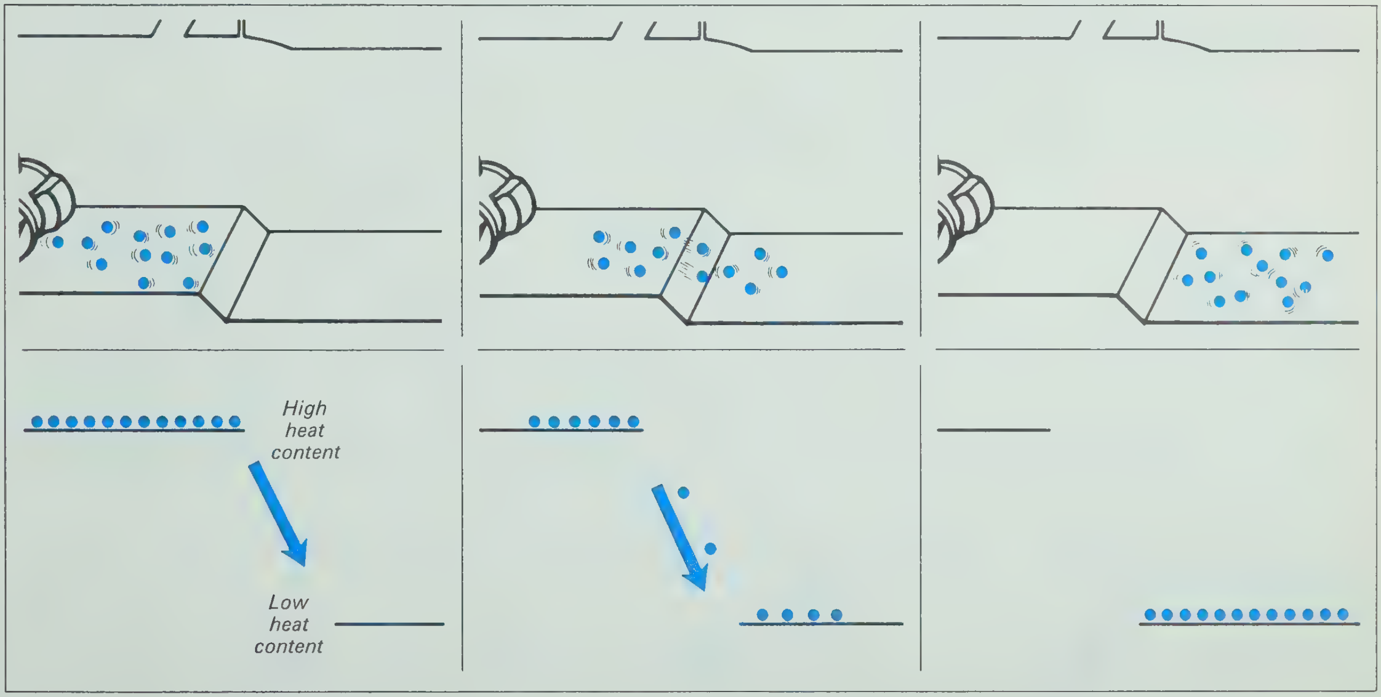


FIGURE 13-12

Comparison of a chemical reaction *to golf balls rolling downhill.*

There are two serious difficulties with our explanation. (Remember "cylindrical objects burn"?) Some endothermic reactions proceed spontaneously. For example, water absorbs heat energy when evaporation occurs. When ammonium chloride dissolves in water, the solution becomes cooler. Again, heat energy is absorbed. In both examples reactions spontaneously "move up an energy hill."

An even more serious difficulty faces us. Spontaneous chemical reactions do not go to completion. Even if a reaction is exothermic, it proceeds only to the equilibrium state.

In our golf ball analogy, "equilibrium" is reached when all of the golf balls are on the lower level. This suggests *all* reactant molecules would be converted to products. Instead we observe that a dynamic equilibrium is established.

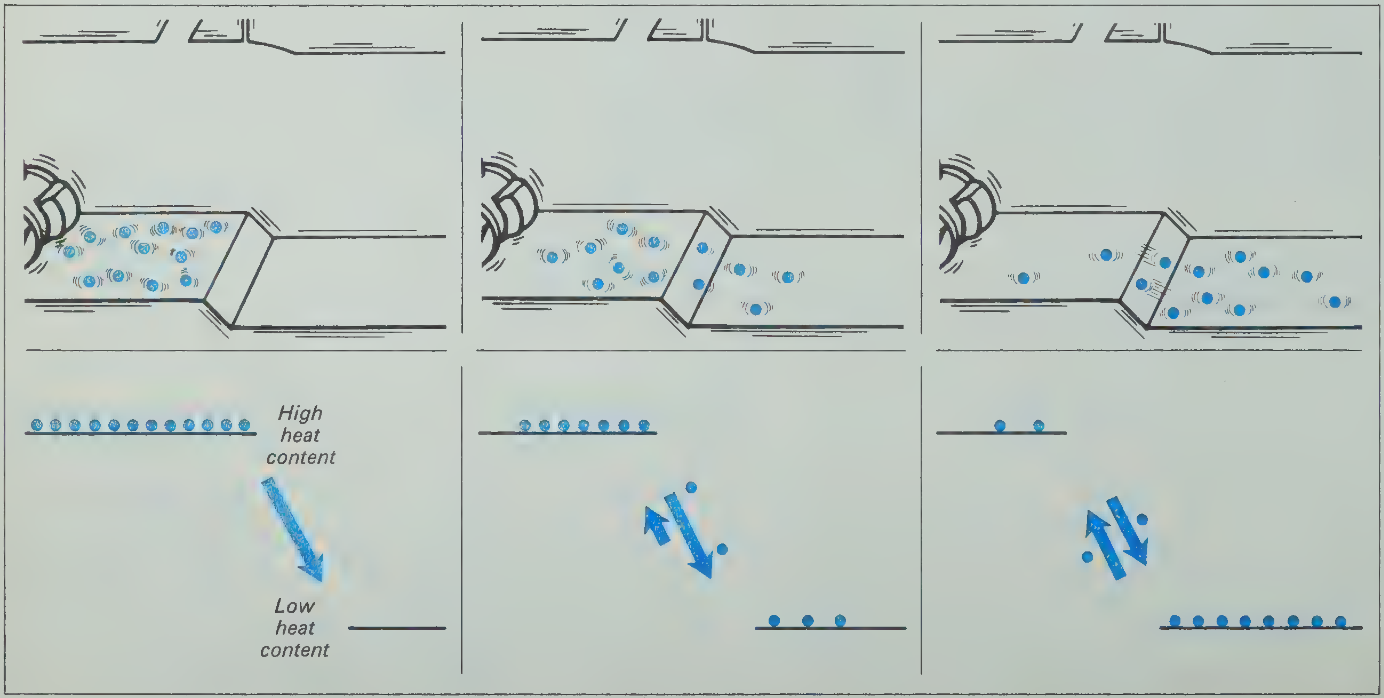
We need to alter our proposed explanation. A new analogy that agrees with the behavior of chemical reactions is needed. How should the golf ball analogy be changed to bring it into better accord with the experimental facts? Here is a possible view.

Suppose the station wagon is driven down a bumpy road. The situation is shown in Figure 13-13.

Now the golf balls are shaken and jostled about. They roll around and collide with each other. Every now and then one of the golf balls accumulates enough energy to return to the upper level of the station wagon floor. Of course, any golf ball that is bounced up tends to roll back down to the lower level a little later. As this bumpy

FIGURE 13-13

Golf balls rolling on the floor of a station wagon *driving on a bumpy road.* The thermal energy drives some molecules "uphill."



ride continues, a state is reached in which golf balls are being jostled up to the higher level at the same rate they are falling back down to the lower level. Then "equilibrium" exists. Some of the golf balls are on the lower level and some on the upper level. Since the rate of rolling up equals the rate of rolling down, a dynamic balance exists.

The analogy solves the problem of the simpler "golf balls roll downhill" picture. The bumpy road model contains a new feature that gives a basis for explaining the spontaneity of some endothermic reactions. What happens if the road becomes smoother? The "jostling up" reaction is less favored. The equilibrium conditions change to favor golf balls on the lower level.

Think of a chemical reaction again. What feature in a reacting chemical system corresponds to the jostling of the bumpy road in our analogy? It is the *temperature.* At any temperature except absolute zero there is a constant random jostling of the molecules. Some molecules have low kinetic energies. Some have high kinetic energies. Occasionally some molecules will get enough energy to "roll uphill" to less stable molecular forms. We encountered a number of examples in the preceding chapter in our discussion of reaction rates. At low temperature very few collisions involved enough energy to reach the top of the activation energy barrier. Increasing the temperature increased the random jostling. The rate of chemical reaction increased.

Now we have an analogy that aids us in understanding chemical reactions and equilibrium. Consider the following features of chemical reactions.

1) *Chemical reactions proceed spontaneously to approach the equilibrium state.*

2) *One factor that fixes the equilibrium state is the energy. Equilibrium tends to favor the state of lowest energy.*

3) *The other factor that fixes the equilibrium state is the randomness implied by the temperature. Equilibrium tends to favor the state of greatest randomness.*

4) *The equilibrium state is a compromise between these two factors: minimum energy and maximum randomness.* At very low temperatures, energy tends to be the more important factor. Then equilibrium favors the molecular substances with the lowest heat content. At very high temperatures, randomness becomes more important. Then equilibrium favors a random distribution among reactants and products without regard for energy differences.

Chemists have found a simple equation that brings these factors together.

$$\Delta G = \Delta H - T\,\Delta S$$

ΔG is called the free energy change for a chemical reaction. It is the net driving energy for the reaction and is the difference between two energy terms, ΔH and $T\,\Delta S$. We have already discussed ΔH, the heat of reaction. ΔH is the potential energy change in a chemical reaction. $T\,\Delta S$ is a new energy term for us. It involves the absolute temperature and ΔS, the entropy change for the chemical reaction. Entropy is a measure of randomness in a system.

At equilibrium the tendency to form products equals the tendency to form reactants. There is no tendency to change. Therefore, the net driving energy must be equal to zero.

$$\Delta G = 0$$

Then we can write:

$$\Delta H = T\,\Delta S$$

At equilibrium there is a balance between two opposing energy terms. The tendency to reach minimum energy (ΔH) equals the tendency to reach maximum randomness ($T\,\Delta S$).

13-16 Review

For a closed system at a uniform temperature, chemical equilibrium is recognized by the constant properties of the system. Chemical equilibrium is a dynamic state in which the rates of the forward and reverse reactions are equal.

Any condition that changes the rates of the reactions involved in the equilibrium system may affect the concentrations of the reactants or products. An important regularity, *Le Chatelier's Principle,* serves as a qualitative guide in predicting how the state of equilibrium is affected when one of the equilibrium conditions is altered.

> *If a closed system at equilibrium is subjected to a change, processes occur that tend to counteract that change.*

The quantitative aspects of chemical equilibrium are expressed in the *Law of Chemical Equilibrium.* The equilibrium law expression has the form

$$K = \frac{[E]^e\,[F]^f}{[A]^a\,[B]^b}$$

for the chemical reaction

$$aA + bB \rightleftarrows eE + fF$$

Solubility calculations show another use of equilibrium expressions.

There are two factors that determine the state of equilibrium. One factor is the energy. *Equilibrium tends to favor the state of lowest energy.* The other factor is the randomness implied by the temperature. *Equilibrium tends to favor the state of greatest randomness.*

The equilibrium state is a *balance* between these two factors: *minimum energy* and *maximum randomness.*

Questions and Problems for Chapter 13

1

Sugar is added to a cup of coffee until no more sugar will dissolve. Does addition of another spoonful of sugar increase the rate at which the sugar molecules leave the crystal phase and enter the liquid phase? Will the sweetness of the liquid be increased by this addition? Explain.

2

Is equilibrium established in a fire burning in a fireplace? Explain.

3

What, specifically, is "equal" in a chemical reaction that has attained a state of equilibrium?

4

One drop of water may or may not establish a state of vapor pressure equilibrium when placed in a closed bottle. Explain.

5

Why are chemical equilibria referred to as "dynamic?"

6

The following chemical equation represents the reaction between hydrogen and chlorine to form hydrogen chloride:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g) + 44.0\ \text{kcal}$$

(a) List four important pieces of information conveyed by this equation.
(b) What are three important areas of interest concerning this reaction for which no information is indicated?

7

Each of the following systems has come to equilibrium. What would be the effect on the equilibrium concentration (increase, decrease, no change) of each substance in the system when the listed reagent is added?

	Reaction	Added Reagent
(a)	$C_2H_6(g) \rightleftharpoons H_2(g) + C_2H_4(g)$	$H_2(g)$
(b)	$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq)$	$CuSO_4(s)$
(c)	$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$	$AgCl(s)$
(d)	$PbSO_4(s) + H^+(aq) \rightleftharpoons Pb^{2+}(aq) + HSO_4{}^-(aq)$	$Pb(NO_3)_2$ solution
(e)	$CO(g) + \frac{1}{2}\,O_2(g) \rightleftharpoons CO_2(g) + \text{heat}$	heat

8

The reaction $CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$ is exothermic, with $\Delta H = -54.1$ kcal/mole. What happens in this system at equilibrium if;

(a) the temperature is increased?
(b) the volume is decreased by a factor of ten?

9

If the phase change represented by

$$\text{Heat} + H_2O(l) \rightleftharpoons H_2O(g)$$

has reached equilibrium in a closed system:

(a) What will be the effect of a reduction of volume, thus increasing the pressure?
(b) What will be the effect of an increase in temperature?
(c) What will be the effect of injecting some steam into the closed system, thus raising the pressure?

10

Methanol (methyl alcohol) can be made according to the following net equation:

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g) + \text{heat}$$

Predict the effect on equilibrium concentrations of an increase in:

(a) Temperature. (b) Pressure.

11

Consider two separate closed systems, each at equilibrium:

(a) HI and the elements from which it is formed.
(b) H_2S and the elements from which it is formed.

What would happen in each system if the total pressure were increased? Assume that conditions are such that all reactants and products are gases.

12

Given:

$$SO_2(g) + \tfrac{1}{2}\,O_2(g) \rightleftharpoons SO_3(g) + 23\text{ kcal}$$

(a) Discuss the conditions that favor a high equilibrium concentration of SO_3.
(b) How many grams of oxygen gas are needed to form 1.00 gram of SO_3?

13

How does a catalyst affect the equilibrium conditions of a chemical system?

14

In any discussion of chemical equilibrium why are concentrations expressed in moles, rather than in grams, per unit volume?

15

Consider the reaction:

$$4\,HCl(g) + O_2(g) \rightleftharpoons 2\,H_2O(g) + 2\,Cl_2(g) + 27\text{ kcal}$$

What effect would the following changes have on the equilibrium concentration of $Cl_2(g)$? Give reasons for each answer.

(a) Increasing the temperature of the reaction vessel.
(b) Decreasing the total pressure.
(c) Increasing the concentration of O_2.
(d) Increasing the volume of the reaction chamber.
(e) Adding a catalyst.

16

Nitric oxide, NO, releases 13.5 kcal/mole when it reacts with oxygen to give nitrogen dioxide. Write the equation for this reaction and predict the effect of (i) raising the temperature, and of (ii) increasing the concentration of NO (at a fixed temperature) on:

(a) the equilibrium concentrations;
(b) the numerical value of the equilibrium constant;
(c) the speed of formation of NO_2.

17

Given:

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

At 450°C, $K = 50.0$ for this reaction. Calculate the equilibrium constant at 450°C if the reaction is written:

$$2\,HI(g) \rightleftharpoons H_2(g) + I_2(g).$$

18

Write the equilibrium expression for the following reactions.

(a) $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$
(b) $CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$
(c) $Zn(s) + 2\,Ag^{+}(aq) \rightleftharpoons Zn^{2+}(aq) + 2\,Ag(s)$
(d) $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^{-}(aq)$
(e) $CN^{-}(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^{-}(aq)$

19

The water gas reaction

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

was carried out at 900°C with the following results.

Trial Number	Partial Pressure, Atm. at Equilibrium			
	CO	H_2O	CO_2	H_2
1	0.352	0.352	0.648	0.148
2	0.266	0.266	0.234	0.234
3	0.186	0.686	0.314	0.314

(a) Write the equilibrium law expression.
(b) Verify that the expression in (a) is a constant, using the data given. See Problem 20.

20

In the reaction

$$2\,\mathrm{HI}(g) \rightleftharpoons \mathrm{H_2}(g) + \mathrm{I_2}(g)$$

at 448°C the partial pressures of the gases at equilibrium are as follows:

partial pressure of HI $= 4.0 \times 10^{-3}$ atm;
partial pressure of H_2 $= 7.5 \times 10^{-3}$ atm;
partial pressure of I_2 $= 4.3 \times 10^{-5}$ atm.

When pressures are properly used in the equilibrium expression, a constant is obtained. What is that constant for this reaction?

21

Reactants *A* and *B* are mixed, each at a concentration of 0.80 mole/liter. They react slowly, producing *C* and *D*: $A + B \rightleftharpoons C + D$. When equilibrium is reached, the concentration of *C* is measured and found to be 0.60 mole/liter. Calculate the value of the equilibrium constant.

Answer: $K = 9.0$.

22

Given:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

At a fixed temperature, what effect would adding more $CaCO_3$ have on the concentration of CO_2 in the region above the solid phase? Explain.

23

Equilibrium constants are given for several systems below. In which case does the reaction as written occur to the greatest extent?

	Reaction	*K*
(a)	$\mathrm{CH_3COOH}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{CH_3COO^-}(aq)$	1.8×10^{-5}
(b)	$\mathrm{CdS}(s) \rightleftharpoons \mathrm{Cd^{2+}}(aq) + \mathrm{S^{2-}}(aq)$	7.1×10^{-28}
(c)	$\mathrm{H^+}(aq) + \mathrm{HS^-}(aq) \rightleftharpoons \mathrm{H_2S}(aq)$	1×10^{7}

24

Write the solubility product expression for each of the following reactions.

(a) $\mathrm{BaSO_4}(s) \rightleftharpoons \mathrm{Ba^{2+}}(aq) + \mathrm{SO_4{}^{2-}}(aq)$
(b) $\mathrm{Zn(OH)_2}(s) \rightleftharpoons \mathrm{Zn^{2+}}(aq) + 2\,\mathrm{OH^-}(aq)$
(c) $\mathrm{Ca_3(PO_4)_2}(s) \rightleftharpoons 3\,\mathrm{Ca^{2+}}(aq) + 2\,\mathrm{PO_4{}^{3-}}(aq)$

25

Write the solubility product expression for each of the following substances in water.

(a) calcium carbonate.
(b) silver sulfide.
(c) aluminum hydroxide.

26

Experiments show that 0.0059 gram of $SrCO_3$ will dissolve in 1.0 liter of water at 25°C. What is K_{sp} for $SrCO_3$?

Answer. 1.6×10^{-9}.

27

The solubility product of AgCl is 1.4×10^{-4} at 100°C. Calculate the solubility of silver chloride in boiling water.

28

How many milligrams of silver bromide dissolve in 20 liters of water? (Use the data given in Table 13-6.)

29

Suppose you add 0.002 mole of solid $Pb(NO_3)_2$ to one liter of 0.001 *M* H_2SO_4. As the lead nitrate dissolves, will lead sulfate precipitate?

30

Suppose 10 ml of 1.0 *M* $AgNO_3$ is diluted to one liter with tap water. If the chloride concentration in the tap water is about 10^{-5} *M*, will a precipitate form?

31

The test described in Problem 30 does *not* give a precipitate if laboratory distilled water is used. What is the maximum chloride concentration that could be present?

32

Will a precipitate exist at equilibrium if 0.5 liter of 2×10^{-3} M $AlCl_3$ solution and 0.5 liter of 4×10^{-2} M sodium hydroxide solution are mixed and diluted to 10^3 liters with water at room temperature?

$$K_{sp} \text{ of } Al(OH)_3 = 5 \times 10^{-33}$$

33

Select from each of the following pairs the more random system.

(a) A brand new deck of cards arranged according to suit and number. The same deck of cards after shuffling.
(b) A box full of sugar cubes.
Sugar cubes thrown on the floor.
(c) A haystack.
Stacked firewood.

34

For each of the following reactions, state: (i) whether tendency toward minimum energy favors reactants or products, (ii) whether tendency toward maximum randomness favors reactants or products.

(a) $H_2O(l) \rightleftarrows H_2O(s) \quad \Delta H = -1.4 \text{ kcal}$
(b) $H_2O(l) \rightleftarrows H_2O(g) \quad \Delta H = +10 \text{ kcal}$
(c) $CaCO_3(s) + 43 \text{ kcal} \rightleftarrows CaO(s) + CO_2(g)$
(d) $I_2(s) + 1.6 \text{ kcal} \rightleftarrows I_2 \text{ (in alcohol)}$
(e) $4\,Fe(s) + 3\,O_2(g) \rightleftarrows 2\,Fe_2O_3(s) + 400 \text{ kcal}$

35

When a solid evaporates directly (without melting), the process is called **sublimation.** Evaporation of solid CO_2 is a familiar example. Two other substances that sublime are FCN and ICN:

$$FCN(s) \rightleftarrows FCN(g) \qquad \Delta H = +5.7 \text{ kcal}$$
$$ICN(s) \rightleftarrows ICN(g) \qquad \Delta H = +14.2 \text{ kcal}$$

(a) In sublimation, does the tendency toward maximum randomness favor solid or gas?
(b) In sublimation, does the tendency toward minimum energy favor solid or gas?
(c) In view of part b, would you expect solid ICN to have a lower or higher vapor pressure than solid FCN at the same temperature?

36

Liquid chloroform, $CHCl_3$, and liquid acetone, CH_3COCH_3, dissolve in each other in all proportions (they are said to be **miscible**).

(a) When pure $CHCl_3$ is mixed with pure acetone, is randomness increased or decreased?
(b) Does the tendency toward maximum randomness favor reactants or products in the reaction

$$CHCl_3(l) + CH_3COCH_3(l) \rightleftarrows 1:1 \text{ solution} \qquad \Delta H = -495 \text{ cal}$$

(c) Considering the sign of ΔH in part b, does the tendency toward minimum energy favor reactants or products?
(d) In view of your answers to parts b and c, discuss the experimental fact that these two liquids are miscible.

Aqueous Acids and Bases

14

You have encountered the words "acid" and "base" a number of times in this course, both in the early chapters of this book and in your laboratory program. In Experiment 8 you dissolved metallic silver in nitric acid; in Experiment 11 you measured the volume of hydrogen gas when a known mass of magnesium metal reacted with hydrochloric acid; and in Experiment 26 you determined the heat of reaction when an acid and a base react. Acids and bases are among the most common and most important chemicals that are found in the laboratory. In addition, a number of acids and bases are often found in our homes: lemon juice owes its sour taste to citric acid; vinegar contains acetic acid; baking soda contains sodium hydrogen carbonate; and household ammonia contains ammonium hydroxide.

In this chapter we will explore how the definitions of acids and bases have changed as chemists searched for regularities and explanations of their experimental results. We will see how the concept of chemical equilibrium provides a way to organize a great deal of information about acids and bases. Most important of all, we will find a way to predict the extent to which an acid-base reaction will occur.

14-1 Operational Definitions of Acids and Bases

Definitions of acids and bases were presented in Section 6-9, page 95, when we discussed electrolytes. **Electrolytes** are substances that dissolve in water to give solutions that conduct electricity. The classification of electrolytes as acids, bases, and salts is based directly on the observed properties of the solutions. These properties provide the simplest definition for each class of compounds. When we classify or define something in terms of "what happens," we are using an **operational definition**. Suppose we encounter a new compound. We can decide whether to call it an acid or a base by carrying out some of the experiments indicated in the definition.

The experimentally observed properties of aqueous acids and bases are summarized below. These lists form the operational definitions of an acid and of a base.

Citric

Acetic

Tartaric

FIGURE 14-1

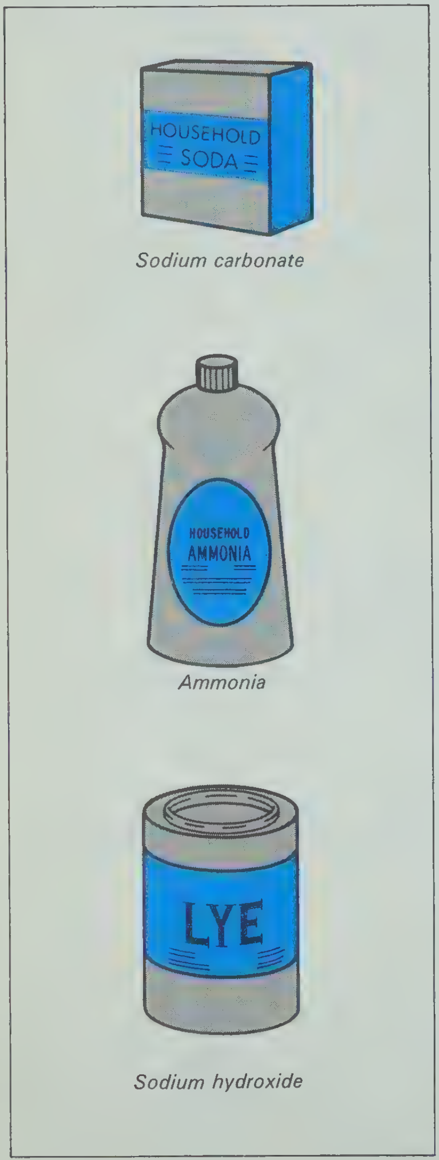
Some familiar acids.

An **acid** is a compound that dissolves in water to give a solution that:

conducts electricity,
reacts with metals such as Zn or Mg, liberating H_2,
changes the color of the dye, litmus, from blue to red,
tastes sour.

A **base** is a compound that dissolves in water to give a solution that:

conducts electricity,
reacts with an acid, to destroy or neutralize its properties,
changes the color of the dye, litmus, from red to blue,
tastes bitter and feels slippery.



Sodium carbonate

Ammonia

Sodium hydroxide

FIGURE 14-2
Some familiar bases.

During the nineteenth century, chemists tried to find explanations for the behavior of acids and bases. They began to replace operational definitions (what happens) with conceptual ones. A **conceptual definition** seeks to identify the causes of observed behavior. The concept underlying the definition often contains ideas of composition and structure.

For many years chemists believed that all acids contain oxygen. When experiments showed that one of the most important acids, hydrochloric acid, contained only hydrogen and chlorine, this belief was abandoned. The generalization that all acids contain hydrogen was then proposed. This change has led to a more valid concept of acids and bases. The Swedish chemist, Svante Arrhenius, provided one of the first definitions of acids and bases that went beyond a cataloguing of experimental observations.

14-2 The Arrhenius Definitions of Acids and Bases

One of the most intriguing questions that challenged Arrhenius and other chemists was "Why do some substances exhibit acidic or basic properties to a greater degree than other substances?" When 1 *M* HCl and 1 *M* acetic acids are compared, we find that the conductivity of the HCl solution is much greater than the conductivity of acetic acid solutions. The rate of reaction of each acid with magnesium or zinc can also be measured. The rate with 1 *M* HCl is much greater than with 1 *M* acetic acid.

Arrhenius proposed conceptual definitions for acids and bases as part of his theory of ionic dissociation. He had suggested that an ionic substance like NaCl(s) dissolved in water to furnish the ions Na^+ and Cl^-. Arrhenius interpreted the high conductivity of electrolyte solutions in terms of ionic movement toward the electrodes.

Arrhenius postulated that *an acid was a substance that dissolved in water to furnish the hydrogen ion, H^+*. Similarly, he called a substance *a base if it could furnish the hydroxide ion, OH^-*. The chemical activity and the electrical conductivity of acidic and basic solutions could be directly related to the degree to which these ions formed when substances dissolved in water.

When an acid such as HCl dissolves in water, almost all of it ionizes. Arrhenius called acids that behaved this way **strong acids.** He represented the chemical reaction with the equilibrium

$$HCl \rightleftarrows H^+ + Cl^- \qquad K \text{ is a large number}$$

When acetic acid dissolves in water, only a small fraction of the molecules ionize. Such an acid is called **a weak acid.** The equilibrium reaction can be written

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^- \qquad K \text{ is a small number}$$

The words *strong* and *weak,* used in this manner, are sometimes confusing. They do *not* refer to the initial concentration of the electrolytes. Instead these words refer to the *degree of ionization.* The information presented in Table 14-1 will help you to see the difference between strong acids and weak acids. Note that each solution is made by dissolving 1.0 mole of the acid in enough water to make 1.0 liter of solution.

TABLE 14-1

Comparison of Strong and Weak Acids

Strong Acid	Weak Acid	Approximate $[H^+]$	Electrical Conductivity	Rate of Reaction with Mg
1.0 M HCl		1 M	High	Fast
1.0 M H_2SO_4		1 M	High	Fast
	1.0 M H_3PO_4	0.1 M	Intermediate	Intermediate
	1.0 M CH_3COOH	0.004 M	Low	Slow

Arrhenius proposed that *strong electrolytes* dissociated almost 100% when dissolved in water. The dissociation of *weak electrolytes* such as CH_3COOH is very small. Very few ions form when CH_3COOH dissolves in water. Arrhenius was able to compare the strengths of acids and bases by measuring the conductivity of solutions. We will discuss acid-base strength in Section 14-7.

The Arrhenius view of acids and bases represented a great advance. However, difficulties began to appear, particularly as chemists' understanding of atomic structure developed. Since the hydrogen atom has only one electron, the ion H^+ must correspond to the nucleus of the atom. Such a small positive ion would interact strongly with electrons on other molecules or ions. This would be particularly true with water molecules, the solvent. A number of different experiments support the idea that the hydrogen ion is hydrated. Some experiments suggest that the hydrogen ion should be represented by the formula H_3O^+. Other experiments indicate that there are more water molecules, corresponding to the formula $H_9O_4^+$. The unhydrated hydrogen ion does not exist to any appreciable extent in water. Some chemists indicate hydration of ions by writing equations in this manner

$$\text{HCl} + \text{water} \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$$
$$\text{CH}_3\text{COOH} + \text{water} \rightleftarrows \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$$

Some chemists prefer to represent these same reactions as

$$\text{HCl}(aq) + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)$$
$$\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O} \rightleftarrows \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$$

Recognition that the solvent plays a direct role in acid-base systems removes another difficulty of the Arrhenius definition. There are other substances like NH_3 and Na_2CO_3 which do not contain hydroxide ion. However, they dissolve in water to form solutions that have the properties associated with bases. The explanation for these observations appears when we write equations which include the solvent.

$$\text{NH}_3(g) + \text{H}_2\text{O} \rightleftarrows \text{NH}_4{}^+(aq) + \text{OH}^-(aq)$$
$$\text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O} \rightleftarrows \text{HCO}_3{}^-(aq) + \text{OH}^-(aq) + 2\,\text{Na}^+(aq)$$

Ammonia and carbonate ions react with the solvent to produce $OH^-(aq)$. The properties of these solutions are similar to the solutions of other bases. These reactions clearly emphasize the important role played by the solvent. Recognition of the importance of the solvent led chemists to propose more general definitions of acids and bases. Before discussing these definitions, it is useful to consider the reaction between an acid and a base, one of the most important reactions in chemistry. It is given a special name, **neutralization.**

14-3 The Neutralization Reaction

We can write the equation for the reaction of hydrochloric acid and sodium hydroxide solutions in several ways. One of them is

$$\text{H}^+(aq) + \text{Cl}^-(aq) + \text{Na}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O} + \text{Cl}^-(aq) + \text{Na}^+(aq)$$

The sodium and chloride ions appear as reactants and products. They do not enter into the neutralization reaction. Ions that are present but do not participate in the reaction are called **spectator ions.** Frequently chemists do not include them in the equation. This procedure simplifies the equation and emphasizes the reaction that is taking place. The result is called a **net ionic equation,** such as

$$\text{H}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}$$

Remember, however, that you cannot find a bottle in the chemical stockroom that contains only $H^+(aq)$ or $OH^-(aq)$ ions!

This reaction must be written as an equilibrium system. Even though the electrical conductivity of pure water is very low, careful measurements show that water is a weak electrolyte. The conductivity measurement indicates that the ions $H^+(aq)$ and $OH^-(aq)$ are present at very low concentrations in pure water.

$$H_2O \rightleftarrows H^+(aq) + OH^-(aq)$$

The equilibrium expression for this system can be written

$$K_w = [H^+][OH^-]$$

The constant K_w is often called the *ion product* for water. The value for K_w at 25°C is 1.00×10^{-14}.

In pure water, every time an $H^+(aq)$ ion forms, an $OH^-(aq)$ ion must form too. Therefore, we know that

$$[H^+] = [OH^-] \qquad \text{(in pure water)}$$

This relationship allows us to write

$$\begin{aligned} K_w &= [H^+][OH^-] = [H^+]^2 \\ [H^+] &= \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}} \\ [H^+] &= 1.0 \times 10^{-7}\,M \qquad \text{(in pure water)} \end{aligned}$$

In addition we can see that

$$[OH^-] = 1.0 \times 10^{-7}\,M \qquad \text{(in pure water)}$$

At equilibrium the ion concentrations are only 10^{-7} *M*. *Water is a weak electrolyte.*

EXERCISE 14-1

Show that the concentration of H_2O in a liter of pure water is 55.5 *M*. Assume that the mass of one liter of water is 1.00×10^3 grams.

EXERCISE 14-2

What is the concentration of H_2O in 1.00×10^2 ml of water? In 1.00 ml?

14-4 The Special Roles of $H^+(aq)$ and $OH^-(aq)$

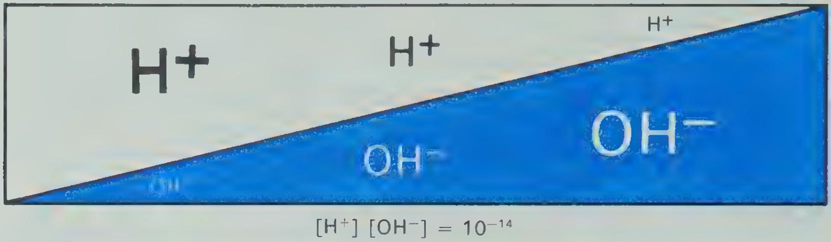
In pure water the concentrations of $H^+(aq)$ and $OH^-(aq)$ are equal. But what happens if some HCl(g) is added? HCl(g) is a strong electrolyte which dissolves to give the hydrated ions, $H^+(aq)$ and $Cl^-(aq)$. All acids increase the $[H^+]$ but not the $[OH^-]$ in the system. The $[H^+]$ and $[OH^-]$ are no longer equal. However experiments show that the equilibrium relation is still valid.

$$K_w = [H^+][OH^-]$$

We can rearrange this equation to show

$$[OH^-] = \frac{K_w}{[H^+]}$$

If $[H^+]$ increases, then $[OH^-]$ must decrease. We represent the relation schematically in Figure 14-3.



$[H^+]\,[OH^-] = 10^{-14}$

FIGURE 14-3

Relation between H^+ and OH^- in aqueous solutions.

Suppose, on the other hand, we add the strong electrolyte NaOH to pure water. The $[H^+]$ and $[OH^-]$ are no longer equal because the base NaOH increases the hydroxide ion concentration without adding to the hydrogen ion concentration. The concentration of $H^+(aq)$ would be given by the relation:

$$[H^+] = \frac{K_w}{[OH^-]}$$

Some examples will give you practice with this concept. Suppose we start with 1.0 liter of pure water. We have just seen that $[H^+] = [OH^-] = 10^{-7}\,M$ in water. Now add 0.1 mole of hydrogen chloride to the water. Since HCl is a strong electrolyte, 0.1 mole will furnish 0.1 mole of $H^+(aq)$ and 0.1 mole of $Cl^-(aq)$. The maximum concentration for $H^+(aq)$ would initially be the sum of $[H^+]$ from water and from HCl.

$$[H^+]_{\text{total}} = [H^+]_{\text{water}} + [H^+]_{\text{HCl}} = 10^{-7}\,M + 10^{-1}\,M$$

The very small amount of $H^+(aq)$ coming from water becomes even smaller in accord with Le Chatelier's Principle. The contribution of H^+ from water is so small it can be neglected. The concentration of hydroxide ion can be calculated easily.

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-1}} = 10^{-13}\,M$$

Addition of 0.1 mole of HCl to a liter of water changes the hydroxide concentration by a factor of a million! Review this example, using Le Chatelier's Principle as a guide. If HCl is added to water, a stress is placed on an equilibrium system. The concentration of $H^+(aq)$ is increased. Reaction between $OH^-(aq)$ and $H^+(aq)$ takes place to relieve the stress. The "box score" can be seen in Table 14-2.

TABLE 14-2

The Concentrations of $H^+(aq)$ and $OH^-(aq)$
When 0.1 mole of HCl Is Added to 1.0 Liter of Water

	Initial Concentrations System at Equilibrium	Hypothetical Situation Immediately After Adding HCl System Not at Equilibrium	Final Concentrations System at Equilibrium
$[H^+]$	10^{-7} *M*	10^{-1} *M* $+ 10^{-7}$ *M*	10^{-1} *M*
$[OH^-]$	10^{-7} *M*	10^{-7} *M*	10^{-13} *M*
$[H^+][OH^-]$	$(10^{-7}) \times (10^{-7}) = 10^{-14}$	not applicable	$(10^{-1}) \times (10^{-13}) = 10^{-14}$

EXERCISE 14-3

Show that the addition of 0.010 mole of solid NaOH to 1.0 liter of water reduces the concentration of $H^+(aq)$ to 1.0×10^{-12} *M*.

EXERCISE 14-4

Suppose that 3.65 grams of HCl are dissolved in 10.0 liters of water. What is the value of $[H^+]$? Show that $[OH^-] = 1.00 \times 10^{-12}$ *M*.

EXERCISE 14-5

How many hydrogen and hydroxide ions would there be in 1 liter of H_2O?

How many hydrogen and hydroxide ions would there be in 1 liter of 0.1 *M* HCl?

The concentrations of $H^+(aq)$ and $OH^-(aq)$ always are related through the equilibrium relation $K_w = [H^+][OH^-]$.

In neutral solutions	$[H^+] = [OH^-]$
In acidic solutions	$[H^+] > [OH^-]$
In basic solutions	$[H^+] < [OH^-]$

The ease with which we can control and vary the concentrations of $H^+(aq)$ and $OH^-(aq)$ is important. These ions take part in many reactions that occur in aqueous solutions. If $H^+(aq)$ is a reactant or a product in a reaction, the variation of the hydrogen ion concentration may have an enormous effect on the reaction. Such variations cause changes in the concentrations of all the reactants and products so that the numerical value of the equilibrium law expression continues to equal the equilibrium constant. Furthermore, there are many reactions for which either the hydrogen ion or the hydroxide ion is a catalyst. An example was discussed in Section 12-8, the decomposition of formic acid catalyzed by sulfuric acid. Formic acid is reasonably stable until the hydrogen ion concentration is raised. Then the rate of decomposition becomes very rapid.

14-5 Acid-Base Titrations

In making quantitative measurements, chemists frequently must determine the concentration of a solution. There are a number of methods to do this. One of the most important is called **titration.** The following discussion illustrates what happens in a titration using the reaction between a strong acid and a strong base as the example.

If 0.1 mole of HCl is dissolved in 100 ml of H_2O, the concentration of hydrogen ion is 1.0 *M*. Addition of small amounts of solid NaOH decreases the concentration of hydrogen ion because of the neutralization reaction:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

Initially the solution is acidic. As more and more NaOH is added, the solution becomes less acidic. When 0.10 mole of NaOH has been added, the solution is neutral. The concentrations of $H^+(aq)$ and $OH^-(aq)$ would then be equal to each other. When equimolar amounts of HCl and NaOH have been mixed in a titration, we say that the **equivalence point** is reached. Now, more NaOH makes the solution basic. Numerical values for the hydrogen and hydroxide concentrations at different points in the titration are summarized in Table 14-3.

TABLE 14-3

The Changes in $[H^+]$ and $[OH^-]$ During the Titration of 100 ml of 1.0 *M* HCl

Initial Number of Moles, HCl	Number of Moles NaOH Added	Excess Number of Moles HCl	or NaOH	$[H^+]$	$[OH^-]$
0.10	0.00	0.10	HCl	1.0	1.0×10^{-14}
0.10	0.09	0.01	HCl	1.0×10^{-1}	1.0×10^{-13}
0.10	0.099	0.001	HCl	1.0×10^{-2}	1.0×10^{-12}
0.10	0.10	none		1.0×10^{-7}	1.0×10^{-7}
0.10	0.101	0.001	NaOH	1.0×10^{-12}	1.0×10^{-2}
0.10	0.11	0.01	NaOH	1.0×10^{-13}	1.0×10^{-1}
0.10	0.20	0.10	NaOH	1.0×10^{-14}	1.0

If we plot the concentration of hydrogen ion as NaOH(s) is added to the solution, the changes during a titration are shown clearly. Figure 14-4 indicates that the change in $[H^+]$ is quite gradual until close to the equivalence point. In the early stages of the titration the $[H^+]$ changes by a factor of 100 when 0.099 mole of NaOH(s) is added. But near the equivalence point, 0.002 mole of NaOH(s) changes the $[H^+]$ from 10^{-2} *M* to 10^{-12} *M*, a factor of 10^{10}.

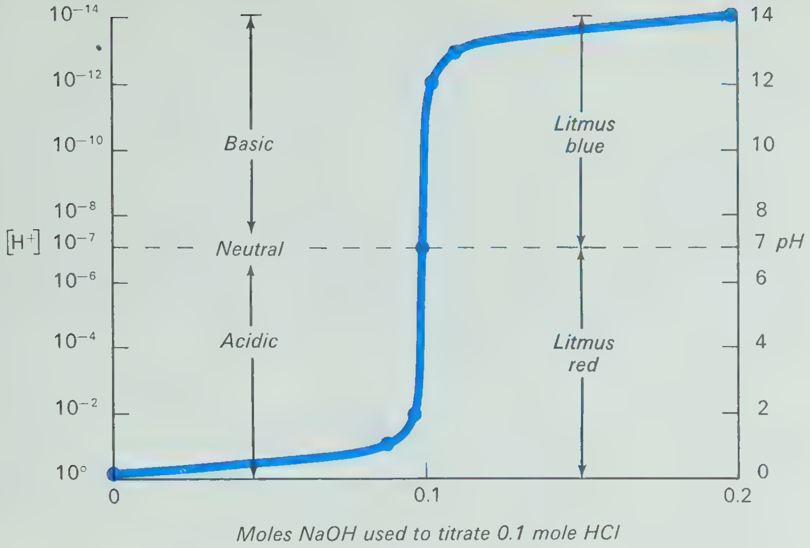


FIGURE 14-4

Titration curve for the reaction of HCl with NaOH.

EXERCISE 14-6

Calculate the $[H^+]$ and $[OH^-]$ for the titration just discussed when 0.0999 mole of NaOH(s) has been added.

There are two aspects of Figure 14-4 that have not been discussed. First, if we add litmus dye at the start of the titration, the color of the solution is red. The solution is acidic. However, the hydrogen ion concentration changes quite rapidly at the equivalence point. The color of the solution suddenly changes to blue. The $[H^+]$ is now less than 10^{-7} *M*; the solution is basic. Substances like litmus are called **indicators.** Indicators are weak acids or bases, which have one color in acid solution and another in basic solution. We can represent how they function by this equilibrium equation:

$$\underset{\text{(color 1)}}{H(Ind)} \rightleftharpoons H^+(aq) + \underset{\text{(color 2)}}{Ind^-(aq)}$$

addition of base ⟶

⟵ addition of acid

The second new aspect in Figure 14-4 is the symbol *p*H in the label on the right side. When dealing with very large or very small numbers, it is often convenient to refer only to the exponent of the number. For example, 10^{-13} could be referred to as 13. The term *p*H is defined as the exponent for the hydrogen ion concentration, with sign changed to give a positive number.

$$pH = x \qquad \text{when} \qquad [H^+] = 10^{-x}$$

Using the *p*H system we see that:

$pH = 7$	for neutral solutions
$pH < 7$	for acidic solutions
$pH > 7$	for basic solutions

EXERCISE 14-7

You have 100 ml of an HCl solution whose concentration you do not know. Titration with 0.10 *M* NaOH solution requires 50 ml of the base to reach the equivalence point. What was the original concentration of the HCl solution?

14-6 The Brønsted-Lowry Definitions of Acids and Bases

In 1923 the Danish chemist, J. N. Brønsted, and the English chemist, T. M. Lowry, independently proposed new conceptual definitions for acids and bases. They proposed that

an acid is a substance that can *donate a proton.*

a base is a substance that can *accept a proton.*

We can write some equations which will show the meaning of these definitions. The acid will be written as the first reactant in each equation. For convenience the notation (aq) after each ion is omitted.

$$HCl(g) + H_2O \longrightarrow H_3O^+ + Cl^-$$
$$CH_3COOH + H_2O \longrightarrow H_3O^+ + CH_3COO^-$$
$$H_2O + NH_3(g) \longrightarrow NH_4^+ + OH^-$$
$$H_2O + CO_3^{2-} \longrightarrow HCO_3^- + OH^-$$

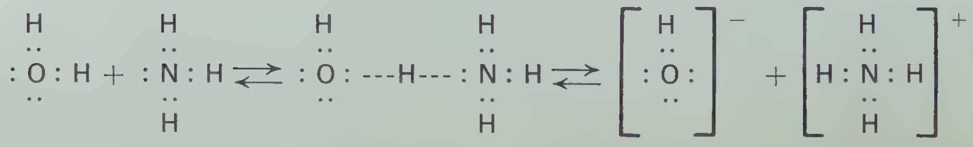
Four important ideas can be derived from these equations.

1. These definitions are not limited to reactions taking place in aqueous solutions. The proton transfer in the reaction

$$HCl(g) + NH_3(g) \longrightarrow NH_4^+ + Cl^-$$

shows that HCl is an acid and NH_3 is a base. According to this definition, NH_4^+ is an acid and Cl^- is a base.

2. A look at the electronic structure of ammonia and water will help us to visualize what is happening and to aid in proposing a reaction mechanism. When collision occurs, we expect an activated complex to be formed:



This mechanism suggests that hydrogen bond formation provides the route for proton transfer. Moreover, this mechanism suggests that the reaction is reversible.

$$H_2O + NH_3 \rightleftarrows OH^- + NH_4^+$$

3. The solvent water plays an important role in the Brønsted-Lowry system. In the first two equations, water acts as a base; water accepts protons. In the last two equations, water acts as an acid; water donates protons.

4. Close inspection of these equations helps us realize that the products in these reactions are acids and bases too.

$$\begin{aligned} CH_3COOH + H_2O &\rightleftarrows H_3O^+ + CH_3COO^- \\ H_2O + NH_3 &\rightleftarrows NH_4^+ + OH^- \\ HB_1 + B_2 &\rightleftarrows HB_2^+ + B_1^- \\ \text{Acid}_1 + \text{Base}_2 &\rightleftarrows \text{Acid}_2 + \text{Base}_1 \end{aligned}$$

Each reaction is reversible. Acetic acid can donate a proton to the base water; the acid H_3O^+ can donate a proton to the base acetate ion, CH_3COO^-. Each pair, $CH_3COOH—CH_3COO^-$ or $H_3O^+—H_2O$, differs only by a proton. They are called **acid-base pairs.**

A strong acid would have large tendency to donate a proton. *The base paired with a strong acid would be a weak base. The base paired with a weak acid would be a strong base.* A strong base has a large tendency to keep a proton.

14-7 The Strengths of Acids and Bases

The equilibria prevailing in acidic and basic solutions can be used to determine the relative strengths of acids and bases. For example, consider the behavior of two weak acids, acetic acid and hydrofluoric acid.

$$\begin{aligned} CH_3COOH + H_2O &\rightleftarrows H_3O^+ + CH_3COO^- \\ HF + H_2O &\rightleftarrows H_3O^+ + F^- \end{aligned}$$

Measurements of the electrical conductivities of 0.10 *M* solutions of these two acids show that there are more ions in the HF solution than in the acetic acid solution. Acetic acid shows less tendency to donate a proton to the base water than hydrofluoric acid does. We can express this tendency quantitatively in equilibrium law expressions for the reactions. For acetic acid,

$$K = \frac{[H_3O^+][CH_3COO^-]}{[H_2O][CH_3COOH]}$$

Since the concentration of H_2O is constant, it is combined with K (see Section 13-11, page 240) to give K_A.

$$K_A = K[H_2O] = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

In a similar way we find for HF,

$$K_A = \frac{[H_3O^+][F^-]}{[HF]} = 6.7 \times 10^{-3}$$

The larger value for the equilibrium constant for HF means that it is a stronger acid than acetic acid. A larger fraction of the HF molecules have formed ions. These ideas can be summarized in terms of a general acid, HB. The acidic nature of HB is related to its ability to donate protons to H_2O.

$$HB + H_2O \rightleftarrows H_3O^+ + B^-$$

The equilibrium constant for this reaction has the form:

$$K_A = \frac{[H_3O^+][B^-]}{[HB]}$$

It is important to recognize that in each of these examples, CH_3COOH, HF, and HB, we are measuring the tendency for the acid to donate a proton to the *same base,* H_2O. This procedure allows us to rank acids in order of their strengths. Table 14-4 is a list of some of the more common acid-base pairs. A more complete tabulation is given in Appendix 3. The larger the value for K_A, the stronger is the acid.

Notice the value $K = 1.00$ for the acid-base pair, H_3O^+ and H_2O. The Brønsted-Lowry definition chooses the base H_2O as the reference in establishing the table of acid strengths. This situation becomes even clearer if the donation of a proton by H_3O^+ to the reference base is written out.

$$H_3O^+ + H_2O \rightleftarrows H_3O^+ + H_2O$$

$$K = \frac{[H_3O^+][H_2O]}{[H_3O^+][H_2O]} = 1$$

EXERCISE 14-8

Which of the following acids is the strongest and which is the weakest? Use Appendix 3 to verify your answer.

nitrous acid	HNO_2	$K_A = 5.1 \times 10^{-4}$
sulfurous acid	H_2SO_3	$K_A = 1.7 \times 10^{-2}$
phosphoric acid	H_3PO_4	$K_A = 7.1 \times 10^{-3}$

TABLE 14-4

Equilibrium Constants for Acids in Aqueous Solution

$$HB + H_2O \rightleftarrows H_3O^+ + B^-$$

Acid-Base Pair Acid	 Base	Relative Strength of Acid	Relative Strength of Base	$K_A = \frac{[H_3O^+][B^-]}{[HB]}$
HCl	Cl^-	↓	↑	Very large
HNO_3	NO_3^-	Very strong	Very	Very large
H_2SO_4	HSO_4^-	↓	weak	Large
H_3O^+	H_2O	Strong	↑	55.5
HSO_4^-	SO_4^{2-}	↓		1.3×10^{-2}
HF	F^-	Weak		6.7×10^{-4}
CH_3COOH	CH_3COO^-			1.8×10^{-5}
H_2CO_3	HCO_3^-			4.4×10^{-7}
H_2S	HS^-			1.0×10^{-7}
NH_4^+	NH_3			5.7×10^{-10}
HCO_3^-	CO_3^{2-}	↓	Weak	4.7×10^{-11}
HS^-	S^{2-}	Very	↑	1.3×10^{-13}
H_2O	OH^-	weak	Strong	1.8×10^{-16}
OH^-	O^{2-}	↓	↑ Very strong	$< 10^{-36}$

Another important aspect of the Brønsted-Lowry definitions for acids and bases is the role of the solvent, H_2O. The strongest acid that can be present at any appreciable concentration in water is H_3O^+. The strongest base that can be present at any appreciable concentration in water is OH^-. Very strong acids like HCl and HNO_3 do not exist as undissociated molecules in H_2O. Similarly, an oxide like Na_2O dissolves in water to form OH^- rather than the very strong base oxide ion, O^{2-}.

$$HCl(g) + H_2O \longrightarrow H_3O^+ + Cl^-$$
$$Na_2O(s) + H_2O \longrightarrow 2\,Na^+ + 2\,OH^-$$

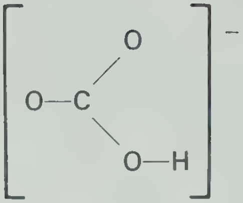
In Table 14-4 acids are not only ranked in order of their tendency to donate protons to the base water, but the acids are also ranked in terms of their tendency to donate protons to any base in aqueous solution. This interpretation guides us in answering a question like this:

> Are reactants or products favored when $Na_2CO_3(s)$ is added to an aqueous solution of HF? The reaction in question is

$$HF + CO_3^{2-} \rightleftarrows HCO_3^- + F^-$$

Looking at Table 14-4, we find equilibrium constants for the two acids:

$$HF + H_2O \rightleftarrows H_3O^+ + F^- \qquad K_A = 6.7 \times 10^{-4}$$
$$HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^{2-} \qquad K_A = 4.7 \times 10^{-11}$$



In aqueous solution HF has a greater tendency to donate a proton to H_2O than HCO_3^- does. The bond in HF is more easily broken than the H—O bond in HCO_3^-. This suggests that HF, the stronger acid, donates a proton to CO_3^{2-}.

Reversing the HCO_3^- reaction, we write

$$HF + H_2O \rightleftarrows H_3O^+ + F^-$$
$$H_3O^+ + CO_3^{2-} \rightleftarrows HCO_3^- + H_2O$$

Combination of these equations now gives the desired net reaction

$$HF + CO_3^{2-} \rightleftarrows HCO_3^- + F^-$$

Since HF is a stronger acid than HCO_3^-, the proton donation from HF to the base CO_3^{2-} is more likely than the proton donation from HCO_3^- to F^-. This must mean that the products of the reaction between Na_2CO_3 and HF are favored. Other examples of this kind suggest a useful regularity:

> *An acid will react with the base of any acid-base pair below it in the table.*

EXERCISE 14-9

Convince yourself that the equilibrium constant for the reaction

$$CO_3^{2-} + H_3O^+ \rightleftarrows HCO_3^- + H_2O$$

is $1/K_A$ where K_A is the equilibrium constant for the reaction

$$HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^{2-}$$

EXERCISE 14-10

Are reactants or products favored in the reaction between CH_3COOH and NH_3? Use the qualitative guide just discussed to answer this question.

The equilibrium constant for the reaction

$$HF + CO_3^{2-} \rightleftarrows HCO_3^- + F^-$$

can be determined by a simple mathematical technique. The equilibrium law expression for the reaction is:

$$K = \frac{[F^-][HCO_3^-]}{[HF][CO_3^{2-}]}$$

If we multiply both numerator and denominator by $[H_3O^+]$, the value of K does not change.

$$K = \frac{[H_3O^+][F^-]}{[HF]} \times \frac{[HCO_3^-]}{[H_3O^+][CO_3^{2-}]}$$

The first factor is K_A for HF. The second factor is $1/K_A$ for HCO_3^-. The equilibrium constant for the reaction is:

$$K = \frac{6.7 \times 10^{-4}}{4.7 \times 10^{-11}} = 1.4 \times 10^{7}$$

14-8 Experimental Determination of K_A

How have chemists determined values for the equilibrium constants in Table 14-4? There are several different methods. Perhaps the easiest one makes use of litmus or other indicators. Indicators change color as the hydrogen ion concentration changes. The method we will outline is based on matching the indicator color in two solutions. If the color is the same in both solutions, we assume the hydrogen ion concentration is the same.

The procedure to be followed is illustrated in Figure 14-5. A set of standard solutions is prepared by dilution of an HCl solution whose concentration is known. The same amount of indicator is added to each of these solutions. The color varies from one test tube to another because the hydrogen ion concentration is different in each solution. The weak acid HF is the acid whose K_A we want to determine. The solution on the right is 0.10 *M* HF. The same amount of indicator has been added to this test tube as was added to the HCl solutions. The color of the HF solution seems to match

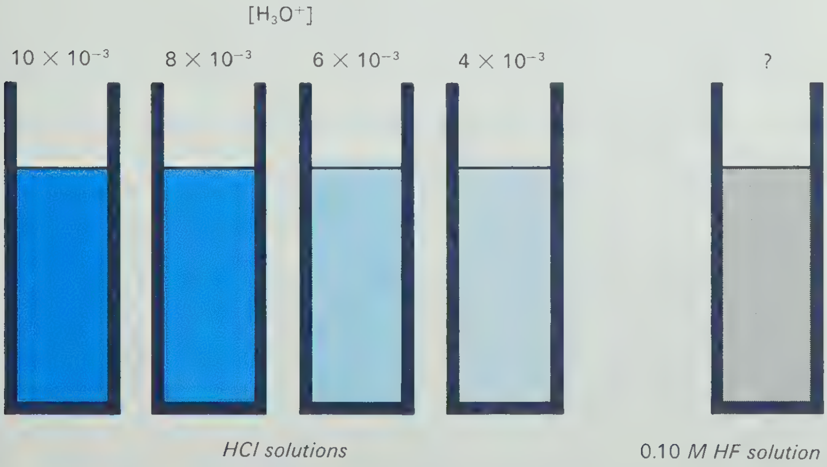


FIGURE 14-5

Using an acid-base indicator to estimate $[H_3O^+]$ in a weak acid solution.

the second HCl test tube, where $[H_3O^+] = 8 \times 10^{-3}$ *M*. Now the K_A for HF can be calculated.

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

$$K_A = \frac{[H_3O^+][F^-]}{[HF]}$$

The balanced equation indicates that the concentration of F^- must be equal to the concentration of H_3O^+. The only source of ions in this example is from the dissociation of HF. Table 14-5 summarizes these results.

TABLE 14-5

Concentrations in a 0.10 *M* HF Solution

Species	Initial Concentration	Equilibrium Concentration	Method Used to Find Concentration
HF	0.10 *M*	$[HF] - [H_3O^+] =$ $0.10 - 0.008 = 0.092$ *M*	Initial concentration from titration with NaOH solution of known concentration. Equilibrium concentration by noting that each H_3O^+ formed uses one HF
H_3O^+	—	8×10^{-3} *M*	Color matching with HCl solutions of known concentration
F^-	—	8×10^{-3} *M*	$[H_3O^+] = [F^-]$

The calculation of K_A is straightforward.

$$K_A = \frac{[H_3O^+][F^-]}{[HF]} = \frac{8 \times 10^{-3} \times 8 \times 10^{-3}}{9 \times 10^{-2}}$$

$$= 7 \times 10^{-4}$$

14-9 Calculations of $[H_3O^+]$

If a value of K_A for an acid is available, we can use it in equilibrium calculations. Here are several examples.

Suppose that a chemist wants to know the hydrogen ion concentration in a solution that was made by dissolving 0.02 mole of acetic acid in enough water to make one liter of solution. Of course, he could go to the laboratory and compare the color of an indicator in his solution with colors of the same indicator in solutions of known hydrogen ion concentration. Or he can calculate the value of $[H_3O^+]$ using the K_A. The equilibrium constant K_A can be found in Table 14-3.

$$K_A = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

The numerical value for K_A is small. This fact tells us that the numerator in the equilibrium expression must be much smaller than the denominator. The chemical reaction is

$$CH_3COOH + H_2O \rightleftarrows H_3O^+ + CH_3COO^-$$

Every time a hydrogen ion forms, an acetate ion forms. Also every time a hydrogen ion forms, an acetic acid molecule must dissociate. We can write:

$$\begin{aligned}[H_3O^+] &= [CH_3COO^-]\\ [CH_3COOH] &= 0.02 - [H_3O^+]\end{aligned}$$

Since the hydrogen ion concentration is very low, we can assume that

$$[CH_3COOH] = 0.02\,M$$

Substituting in the equilibrium expression gives

$$K_A = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H_3O^+][H_3O^+]}{0.02} = 1.8 \times 10^{-5}$$

$$\begin{aligned}[H_3O^+]^2 &= 0.02 \times 1.8 \times 10^{-5} = 36 \times 10^{-8}\\ [H_3O^+] &= 6 \times 10^{-4}\,M\end{aligned}$$

The concentration of H_3O^+ is very low. Our assumption that $[CH_3COOH] = 0.02\,M$ is a reasonable one.

As another example, suppose a solution is made by adding 0.10 mole of CH_3COOH and also 0.20 mole of CH_3COONa, sodium acetate, to enough water to make one liter of solution. Sodium acetate is a strong electrolyte, so that the concentration of acetate ion from this source would be 0.20 *M*. The reaction we must consider is the same as the one in our first example.

$$\begin{aligned}CH_3COOH + H_2O &\rightleftarrows H_3O^+ + CH_3COO^-\\ [CH_3COO^-] &= 0.20 + [H_3O^+]\\ [CH_3COOH] &= 0.10 - [H_3O^+]\end{aligned}$$

Every time an acetic acid molecule dissociates, its concentration decreases. On the other hand, the concentration of CH_3COO^- increases. As in our first example, for every H_3O^+ there will be one CH_3COO^- formed. We anticipate that $[H_3O^+]$ is quite small and we will assume that

$$\begin{aligned}[CH_3COO^-] &= 0.20\,M\\ [CH_3COOH] &= 0.10\,M\end{aligned}$$

Using the equilibrium expression, we find that

$$K_A = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{0.20 \times [H_3O^+]}{0.10} = 1.8 \times 10^{-5}$$

$$[H_3O^+] = 9.0 \times 10^{-6}\ M$$

Our assumption is quite reasonable. The hydrogen ion concentration is very small.

14-10 Acidic and Basic Properties of the Third Row Elements

As a final topic in this chapter, we will consider the acid-base behavior of the hydroxides of the third row elements. The following general formula will be useful.

$$\mathrm{M{-}O{-}H} \qquad \text{or} \qquad \mathrm{M : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : H}$$

Here M represents an element from the third row plus unspecified oxygen and OH groups. The formula shows only one hydroxide to focus our attention on which bond breaks. According to the Arrhenius definitions for acids and bases, compounds with this structure can act as acids if the MO—H bond breaks. On the other hand, such compounds act as bases if the M—OH bond breaks. There is a tug-of-war between M and H for the oxygen atom. There is competition between M^+ and H^+ for the electrons of oxygen.

$$\mathrm{M : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : H} \rightleftharpoons \left[\mathrm{M : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} :}\right]^- + \mathrm{H^+}$$

$$\mathrm{M : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : H} \rightleftharpoons \mathrm{M^+} + \left[\mathrm{: \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} :}\right]\mathrm{H}^-$$

According to Brønsted and Lowry, these same reactions can be described in terms of proton donation.

$$\mathrm{M{-}O{-}H} + H_2O \rightleftharpoons H_3O^+ + \mathrm{M{-}O^-}$$

$$H_2O + \mathrm{M{-}O{-}H} \rightleftharpoons \mathrm{M(OH_2)^+} + OH^-$$

$$A_1 + B_2 \rightleftharpoons A_2 + B_1$$

$\mathrm{M(OH_2)^+}$ can also be written as $\mathrm{M(aq)^+}$.

The only factor that changes in these reactions is the element in the group M. Is there any regularity among the elements that would help us decide whether M—O—H would behave as an acid or a base? Perhaps the trend in ionization energies for the elements Na to Cl can guide us in answering this question. At best this trend may be useful in a qualitative manner only. Remember that ionization energy is measured for an element in the gas phase. Application of ionization energy to aqueous systems may overlook other important factors.

The elements on the left of the Periodic Table have relatively low ionization energies and those on the right have relatively high ionization energies. This suggests that for Na and Mg, electrons would be "released" to oxygen. The compounds NaOH and $Mg(OH)_2$ should be strong bases

$$H_2O + M—O—H \rightleftharpoons M(OH_2)^+ + OH^-$$

In contrast to this behavior, the ionization energy is high if M is S or Cl. The tendency for M to attract electrons from the oxygen atom would be very large. The oxygen atom would be less able to bind the proton.

$$M—O—H + H_2O \rightleftharpoons H_3O^+ + MO^-$$

The compounds H_2SO_4 and $HClO_4$ should be strong acids.

What is found for Al, Si, and P? We might expect their compounds with the M—O—H structure to have properties intermediate to those of the strong acids and bases. The acidic and basic properties for the third row elements are summarized in Table 14-6.

TABLE 14-6

Trends in Acid or Base Strength
for the Third Row Elements

Name	Formula	Acid or Base Strength
Sodium hydroxide	NaOH	Strong base
Magnesium hydroxide	$Mg(OH)_2$	Strong base
Aluminum hydroxide	$Al(OH)_3$	Very weak acid and very weak base
Silicic acid	$Si(OH)_4$ or H_4SiO_4	Very weak acid
Phosphoric acid	$OP(OH)_3$ or H_3PO_4	Weak acid
Sulfuric acid	$O_2S(OH)_2$ or H_2SO_4	Strong acid
Perchloric acid	$O_3Cl(OH)$ or $HClO_4$	Very strong acid

The ionization energy increases from left to right in the Periodic Table. Attraction of electrons by M increases. As electrons are withdrawn from the O—H bond, the bond weakens and the tendency to release the proton increases. Acid strength increases.

In this group of elements, aluminum hydroxide is listed both as a very weak acid and as a very weak base. How can this be? Aluminum hydroxide can donate a proton (acting as an acid) or it can accept a proton (acting as a base). Any substance that acts as an acid under some conditions and as a base under other conditions is said to be **amphiprotic.** (Perhaps some of you are ambidextrous, able

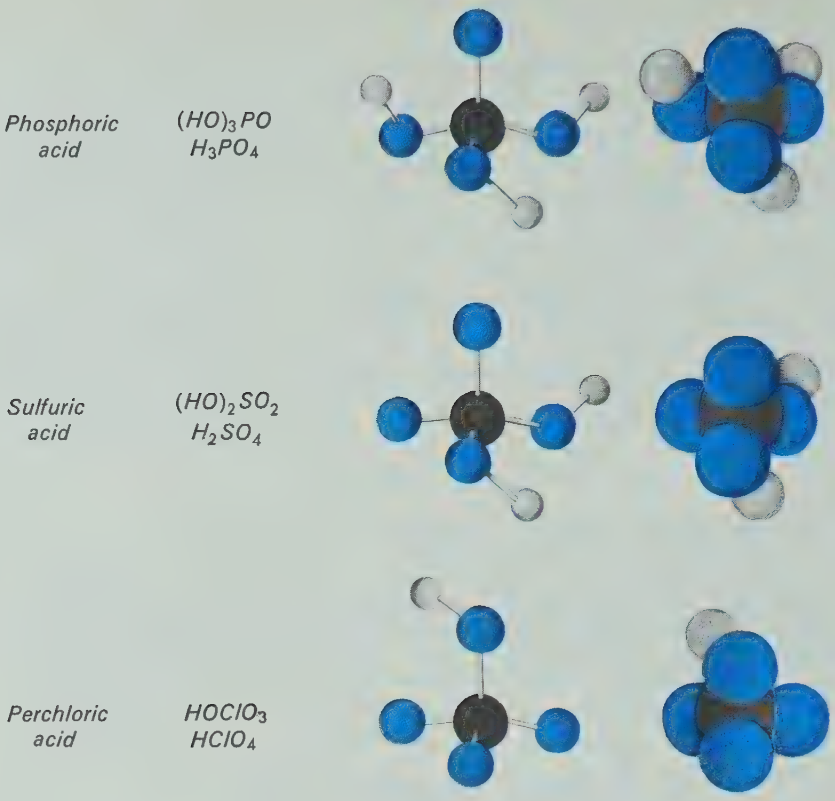


FIGURE 14-6

Structures of H_3PO_4, H_2SO_4, and $HClO_4$.

to use either your right or left hand in writing or in throwing a baseball.) Aluminum hydroxide is a white gelatinous material, with very low solubility in water. Its amphiprotic nature is demonstrated by the fact that $Al(OH)_3$ dissolves either in acids or in bases.

$$3\,H_3O^+ + Al(OH)_3 \rightleftharpoons Al^{3+} + 6\,H_2O$$
$$Al(OH)_3 + OH^- \rightleftharpoons AlO_2^- + 2\,H_2O$$

14-11 Review

In this chapter we have seen how equilibrium principles can be applied to acid-base systems. We began by defining acids and bases in terms of the properties of their aqueous solutions. This **operational** approach is very useful. It tells what experiments to carry out to decide whether a substance should be classed as an acid or as a base.

Arrhenius was the first chemist to offer an explanation for the behavior of acids and bases. According to Arrhenius, an acid was a substance that released H^+, a base released OH^-. Later Brønsted and Lowry proposed a broader definition in which they explained the behavior of acids and bases in terms of proton transfer.

An **acid** is a substance that can *donate a proton.*

A **base** is a substance that can *accept a proton.*

Not only does this point of view develop the important role of the solvent but also it leads to an ordering of acids in terms of their tendency to donate protons to the reference base, H_2O. The equilibrium constants for these reactions offer a method for dealing with acids and bases on a quantitative basis.

The equilibrium expression for water

$$K_w = [H^+][OH^-]$$

emphasizes the importance of water in acid-base systems. In addition, the concentrations of H^+ and OH^- can be controlled easily. These ions take part in many important reactions that occur in aqueous solutions, often influencing the state of equilibrium or the rate of a reaction.

There are still other definitions that chemists have proposed for acids and bases. We have not discussed them in this chapter. It is important for you to realize that these definitions complement each other. A chemist finds it convenient to use one set of definitions in some of his work but another set when he deals with other systems. It is easy for us to forget that much of the chemistry on this planet is tied intimately to the solvent, H_2O. If you met a chemist from another planet, his definitions for acids and bases might be linked to a different solvent.

Questions and Problems for Chapter 14

1

Vinegar, lemon juice, and curdled milk, all taste sour. What other properties would you expect them to have in common?

2

Give the name and formula of three hydrogen-containing compounds that are not classified as acids. State for each compound one or more properties common to acids that it does not possess.

3

Devise an operational and also a conceptual definition of a gas.

4

At 20°C, 0.009 g of $Mg(OH)_2$ will dissolve to make a liter of saturated solution. The magnesium hydroxide that dissolves also ionizes. Is $Mg(OH)_2$ a strong or weak electrolyte? Determine $[OH^-]$.

5

What will happen to the equilibrium

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

as OH^- ions are added? Even though CH_3COOH is a weak acid, one mole of it will require how many moles of OH^- for neutralization?

6

As a solution of barium hydroxide is mixed with a solution of sulfuric acid, a white precipitate forms and the electrical conductivity decreases markedly. Write equations for the reactions that occur and account for the conductivity change.

7

What is the concentration of $H^+(aq)$ in an aqueous solution in which $[OH^-] = 1.0 \times 10^{-3}\ M$?

8

The 100 ml of the HCl solution described in Exercise 14-7 (page 264) is diluted with water to 1.00 liter. What is the concentration of $H^+(aq)$? What is $[OH^-]$ in this solution?

9

An eyedropper is calibrated by counting the number of drops required to deliver 1.0 ml. Twenty drops are required?

(a) What is the volume of one drop?
(b) Suppose one such drop of 0.20 *M* HCl is added to 100 ml of water. What is $[H^+]$?
(c) By what factor did $[H^+]$ change when the one drop was added?

Answer: (c) H^+ increased 1000-fold.

10

Suppose drops of 0.10 *M* NaOH are added, one at a time, to 100 ml of 0.20 *M* HCl. See Problem 9 for description of the dropper.

(a) What will be $[H^+]$ after one drop is added?
(b) What will be $[H^+]$ after two drops are added?
(c) What will be $[H^+]$ after three drops are added?

11

Calculate $[H^+]$ and $[OH^-]$ in a solution made by mixing 50.0 ml 0.200 *M* HCl and 49.0 ml 0.200 *M* NaOH.

Answer: $[OH^-] = 5 \times 10^{-12}\ M$.

12

Calculate $[H^+]$ and $[OH^-]$ in a solution made by mixing 50.0 ml 0.200 *M* HCl and 49.9 ml 0.200 *M* NaOH.

13

How much more 0.200 *M* NaOH solution must be added to the solution in Problem 12 to change $[H^+]$ to $10^{-7}\ M$?

14

If the *p*H of a solution is 5, what is $[H^+]$? Is the solution acidic or basic?

15

What is $[H^+]$ in a solution of $p\text{H} = 8$? Is the solution acidic or basic? What is $[OH^-]$ in the same solution?

16

An acid is a substance H*B* that can form $H^+(aq)$ in the equilibrium:

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq)$$

(a) Does equilibrium favor reactants or products for a strong acid?
(b) Does equilibrium favor reactants or products for a very weak acid?
(c) If acid HB_1 is a stronger acid than acid HB_2, is K_1 a larger or smaller number than K_2?

$$K_1 = \frac{[H^+][B_1^-]}{[HB_1]} \qquad K_2 = \frac{[H^+][B_2^-]}{[HB_2]}$$

17

(a) Which of the following acids is the strongest and which is the weakest?

ammonium ion, NH_4^+ (in an NH_4Cl solution);
hydrogen sulfate ion, HSO_4^- (in a $KHSO_4$ solution),
hydrogen sulfide, H_2S.

(b) If 0.1 *M* solutions are made of NH_4Cl, $KHSO_4$, and H_2S, in which will $[H^+]$ be highest and in which will it be lowest?

18

From a study of Appendix 3, what generalization can you make concerning acids which contain more than one atom of hydrogen in their molecules or ions?

19

When sodium acetate, CH_3COONa, is added to an aqueous solution of hydrogen fluoride, HF, a reaction occurs in which the weak acid HF loses H^+.

(a) Write the equation for the reaction.
(b) What base is competing with F^- for H^+?

20

(a) Write the equation for the reaction that shows the acid-base reaction between hydrogen sulfide, H_2S, and carbonate ion, CO_3^{2-}.

(b) What are the two bases competing for H^+?
(c) From the values of K_A for these two acids, predict whether the equilibrium favors reactants or products.

Answer: (c) Products.

21

Write the equations for the reaction between each of the following acid-base pairs. For each reaction, predict whether reactants or products are favored (using values of K_A given in Appendix 3).

(a) $HNO_2(aq) + NH_3(aq) \rightleftharpoons$
(b) $NH_4^+(aq) + F^-(aq) \rightleftharpoons$
(c) $C_6H_5COOH(aq) + CH_3COO^-(aq) \rightleftharpoons$

22

Write the equations for the reactions between each of the following acid-base pairs. For each reaction, predict whether reactants or products are favored.

(a) $H_2SO_3(aq) + HCO_3^-(aq) \rightleftharpoons$
(b) $H_2CO_3(aq) + SO_3^{2-}(aq) \rightleftharpoons$
(c) $H_2SO_3(aq) + SO_3^{2-}(aq) \rightleftharpoons$

23

A 0.25 *M* solution of benzoic acid (symbolize it H*B*) is found to have $[H^+] = 4 \times 10^{-3}$ *M*. Assuming the simple reaction

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq),$$

calculate K_A for benzoic acid.

24

If 23 grams of formic acid, HCOOH, are dissolved in 10.0 liters of water at 20°C, the $[H^+]$ is found to be 3.0×10^{-3} *M*. Calculate K_A.

25

A chemist dissolved 30 grams of CH_3COOH in enough water to make one liter of solution. What is the concentration of this acetic acid solution? What is the concentration of $H^+(aq)$? Assume a negligible change in $[CH_3COOH]$ because of dissociation of $H^+(aq)$.

26

(a) Nitric acid is a very strong acid. What is $[H^+]$ in a 0.050 *M* HNO_3 solution?
(b) Hydrogen peroxide, H_2O_2, is a very weak acid. What is $[H_2O_2]$ in 0.050 *M* H_2O_2 solution?

27

A water solution that contains 0.10 *M* HF is 8% dissociated. What is the value of its K_A?

Answer: 6.9×10^{-4}.

28

Is the reaction $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O$ exothermic or endothermic? Use your answer and Le Chatelier's Principle to decide whether K_w increases or decreases with increasing temperature.

29

A solution containing 0.20 *M* H_3PO_3, phosphorous acid, is tested with indicators and the $H^+(aq)$ concentration is found to be 5.0×10^{-2} *M*. Calculate the K_A of H_3PO_3, assuming that a second proton cannot be removed.

Oxidation and Reduction

15

Chemists use the words oxidation and reduction to describe certain kinds of chemical reactions. There is a very close comparison between acid-base reactions, discussed in Chapter 14, and oxidation-reduction reactions which are the subject of this chapter. There are many familiar examples of this type of chemical reaction. Here are a few.

- Wood burning in a campfire.
- Gasoline reacting with oxygen in an automobile engine.
- Killing harmful bacteria by adding chlorine to drinking water supplies.
- The corrosion of metals.
- Bleaching hair with hydrogen peroxide.

Lead storage batteries in cars and dry cells in a flashlight are examples of electrochemical cells that are very useful. The chemical changes in these cells involve oxidation and reduction. When you changed the dry cells in a flashlight because the old ones were dead, did you wonder what happened inside the cell? Why does electric current flow from a new dry cell but not from one that has been used many hours? These are important questions in chemistry. By studying the chemical reactions that occur in an electrochemical cell, we will see what chemists mean by the terms oxidation and reduction. More important, we will find a basis for predicting whether reactants or products are favored in an oxidation-reduction system.

15-1 The Chemistry of Electrochemical Cells

A good way to investigate what happens in an electrochemical cell is to build one. A dilute solution of copper sulfate is placed in one beaker. Another beaker contains a dilute solution of silver nitrate. A copper strip is put in the $CuSO_4$ solution and a silver rod in the $AgNO_3$ solution. With a wire, the copper strip is connected to one terminal of an ammeter which measures electric current. The other terminal of the ammeter is connected through a resistor to the

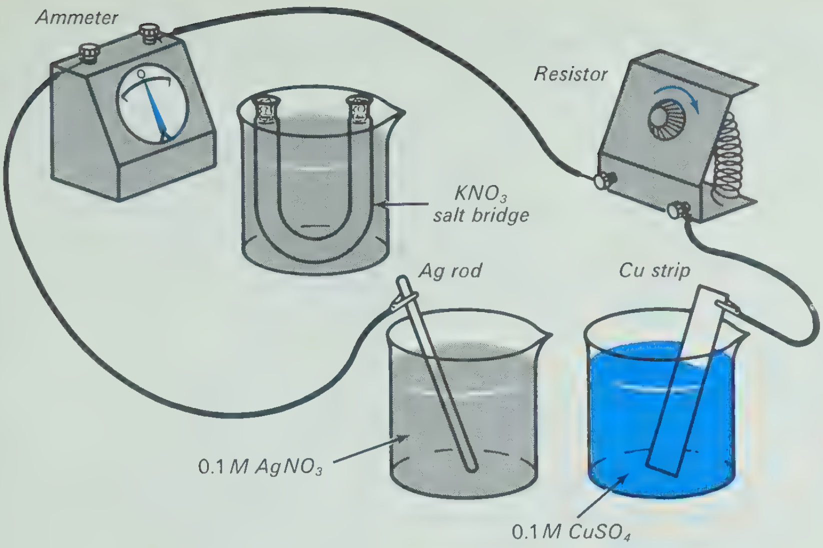

Ammeter
Resistor
KNO_3 salt bridge
Ag rod
Cu strip
0.1 M $AgNO_3$
0.1 M $CuSO_4$

FIGURE 15-1

Apparatus for an electrochemical experiment. The circuit is incomplete because the solutions are not connected.

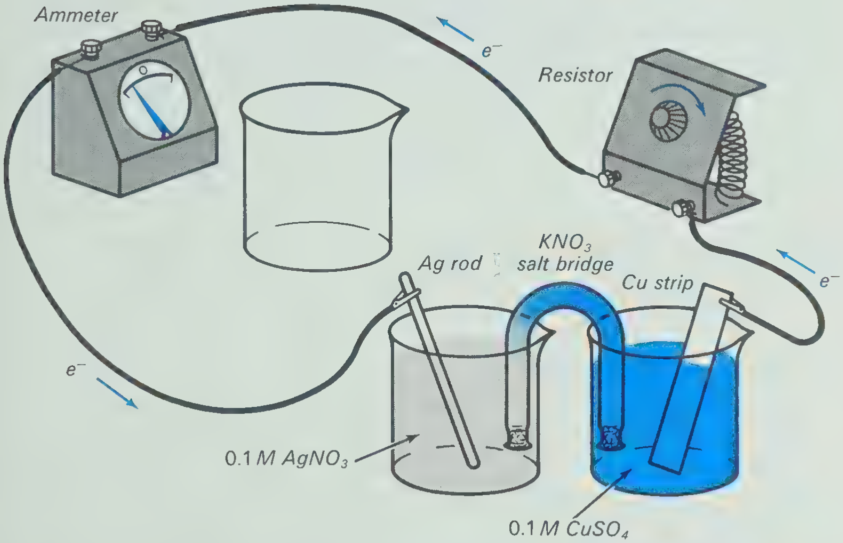

Ammeter
e^-
Resistor
KNO_3 salt bridge
Ag rod
Cu strip
e^-
e^-
0.1 M $AgNO_3$
0.1 M $CuSO_4$

FIGURE 15-2

An electrochemical experiment in progress. The salt bridge connects the solutions and completes the circuit.

silver rod. To complete the electric circuit, connection between the two solutions must be made. One way of doing this is shown in Figures 15-1 and 15-2. A glass U-tube is filled with a solution of a strong electrolyte, usually KNO_3 or NH_4Cl. This tube is called a **salt bridge**. When the salt bridge is put in place, the ammeter needle moves. Electric current moves through the circuit.

The copper strip gets smaller and the silver rod grows. Apparently a chemical reaction takes place. As time goes by, the ammeter shows less and less current flow until, finally, there is none.

How much did the silver rod increase in mass and how much did the copper strip decrease? Let us repeat the experiment, recording the mass of the metal pieces before and after the experiment. One set of data indicates the mass of the copper strip has decreased 0.635 gram. The mass of the silver rod has increased 2.16 grams. This information is more useful when expressed in moles.

$$\text{Moles of Cu reacting} = \frac{\text{Decrease in mass of Cu strip}}{\text{Molar mass of Cu}}$$
$$= \frac{0.635\text{ g}}{63.5\text{ g/mole}}$$
$$= 0.0100\text{ mole}$$
$$\text{Moles of Ag reacting} = \frac{\text{Increase in mass of Ag rod}}{\text{Molar mass of Ag}}$$
$$= \frac{2.16\text{ g}}{108\text{ g/mole}}$$
$$= 0.0200\text{ mole}$$

A simple relation exists between the amounts of copper and silver involved in the reaction. One mole of copper goes into solution for every two moles of silver deposited on the silver rod.

Here is a proposal that may explain these results. Cupric ions, Cu^{2+}, form as atoms of copper release electrons to the wire. The electrons move through the external circuit, through the ammeter and the resistor, to the silver rod in the other beaker. The positively charged silver ions in solution draw electrons from the silver rod and become neutral silver metal atoms. These processes can be summarized:

In the beaker on the right, $Cu(s) \longrightarrow Cu^{2+} + 2\,e^-$

In the beaker on the left, $2\,Ag^+ + 2\,e^- \longrightarrow 2\,Ag(s)$

Adding gives the net equation

$$Cu(s) + 2\,Ag^+ \longrightarrow Cu^{2+} + 2\,Ag(s)$$

This reaction describes what goes on in the entire electrochemical cell. In half of the cell, copper metal dissolves to form Cu^{2+} ions. In the other half of the cell, metallic silver is deposited. Each of these reactions is called a **half-cell reaction,** or more simply, a **half-reaction.**

There are several important ideas presented in these half-reactions.

(1) In this electrochemical cell, two reactions occur in separate beakers. The changes can be considered as two separate reactions. *Equations for the two half-reactions can be written separately.*

(2) *Electrons are written as part of the equation for each half-reaction.* The ammeter shows that electrons move through the circuit. They flow when the reaction starts and do not flow when the reaction stops. The fact that the copper strip loses mass and becomes Cu^{2+} while Ag^+ ion is converted to Ag metal gives us a means of deducing the direction of electron flow through the external circuit.

(3) *New chemical species are produced in each half of the cell.* The copper strip is converted to copper ions (the strip loses mass, the solution becomes bluer). Silver ions are changed to metal (the silver rod gains mass). The new species can be explained in terms of electron gain by silver ions and electron loss by copper atoms.

(4) *The two equations, when combined, express the overall net equation.*

$$\mathrm{Cu(s)} + 2\,\mathrm{Ag}^{+} \longrightarrow \mathrm{Cu}^{2+} + 2\,\mathrm{Ag(s)}$$

The net equation shows that the number of moles of electrons lost by copper atoms exactly balances the number of moles of electrons gained by silver ions.

You may be wondering why there are no electrons shown in the net equation. Electrical measurements indicate that the reaction mixture always remains electrically neutral. *The number of electrons lost must equal the number of electrons gained.* Since there is no net production or consumption of electrons, they do not appear in the equation for the overall reaction. The reaction that occurs in an electrochemical cell is conveniently described using two equations for the half-reactions. In one, electrons are lost; in the other, electrons are gained. To distinguish these half-reactions, two identifying names are helpful.

Oxidation occurs in the half-reaction in which electrons are lost. Copper is oxidized to cupric ions.

$$\mathrm{Cu(s)} \longrightarrow \mathrm{Cu}^{2+} + 2\,e^{-}$$

Reduction occurs in the half-reaction in which electrons are gained. Silver ions are reduced to metal.

$$2\,\mathrm{Ag}^{+} + 2\,e^{-} \longrightarrow 2\,\mathrm{Ag(s)}$$

The overall reaction is called an *oxidation-reduction* or a *redox reaction.*

It may seem strange that an electron gain can be called a reduction! The name for this type of chemical reaction was invented many years ago, long before anyone knew about electrons. Early metallurgists would "reduce" large piles of ore to small piles of metal. *They reduced the ore to metal.* Certainly the meaning of the word is quite clear when used in this manner. Years later, chemists suggested a conceptual definition for reduction: a gain of electrons.

Electrons enter and leave the cell through electrical conductors called **electrodes.** In the example, oxidation takes place at the copper electrode. *The electrode where oxidation occurs is called the* **anode.** Negative charge leaves this electrode as electrons move through the external circuit. Positive charge, in the form of Cu^{2+} ions, is produced in this half of the cell. How is electrical

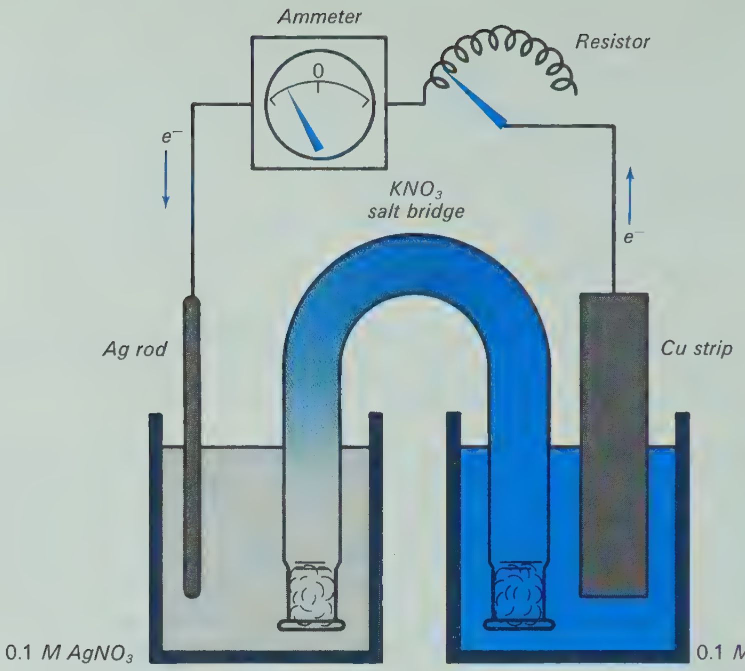


FIGURE 15-3

Schematic diagram of Cu-Ag electrochemical cell.

neutrality of the solution maintained? Movement of ions through the solution provides an explanation. Negative ions drift towards the anode and positive ions move away from the anode. Negative ions are called **anions** because they move towards the anode.

The other half-cell consists of a silver electrode in a solution of silver nitrate. Negative charge arrives at this electrode as electrons move through the external circuit. At the surface of this electrode, electrons encounter Ag^+ ions in the solution. There is a chemical reaction: silver metal is formed. Reduction takes place at the silver electrode. *The electrode where reduction takes place is called the* **cathode.** The reaction $Ag^+ + e^- \longrightarrow Ag$ removes positive charge from the solution. Electrical neutrality is achieved as negative ions drift out of this half-cell and positive ions move into it. Positive ions are called **cations** because they move towards the cathode.

The importance of the salt bridge becomes apparent. As the cell begins to operate, an excess of positive charge builds up in the vicinity of the copper electrode, the anode. A deficiency in positive charge builds up near the silver cathode. The negative anions, in solution and in the salt bridge, start to drift towards the anode. The positive cations, in solution and in the salt bridge, start to move towards the cathode. Negative electric charge is carried away from the copper anode through the external circuit to the silver electrode. *Anions carry negative electric charge through the solutions and the salt bridge back to the copper anode.* The circuit is complete and an electric current is generated. Figure 15-3 shows the same operating cell as Figure 15-2 but in the schematic fashion we will use throughout this chapter.

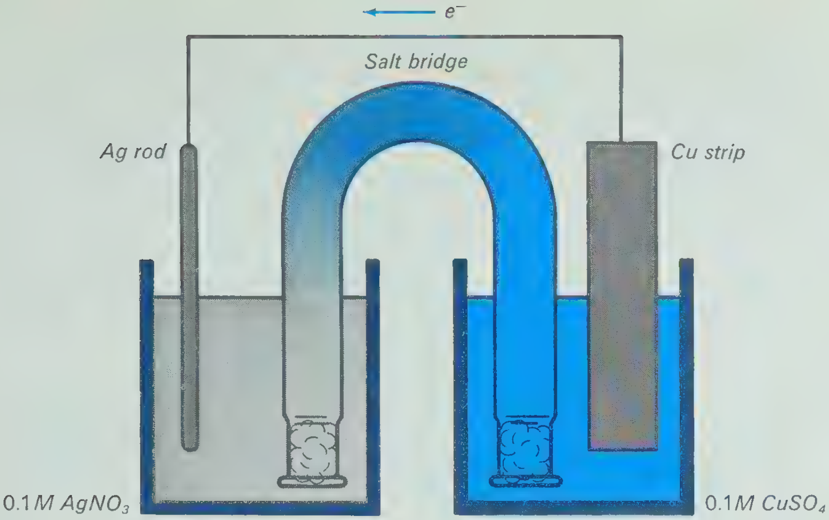

e⁻
Salt bridge
Ag rod
Cu strip
0.1 M AgNO₃
0.1 M CuSO₄

FIGURE 15-4

An electrochemical cell in which the electrodes are joined by a good conductor.

15-2 Oxidation-Reduction Reactions in a Beaker

It is not necessary to set up an electrochemical cell in order to study an oxidation-reduction reaction. A series of figures explains this point. Figure 15-4 shows the first experiment. Instead of the external circuit, with ammeter and resistor, the electrodes have been

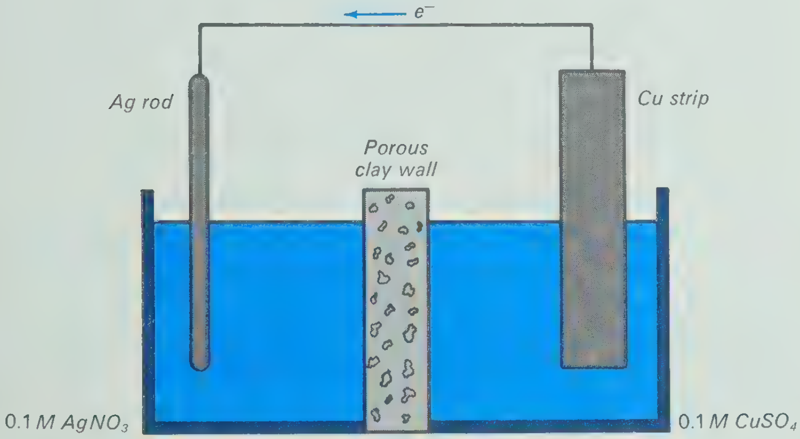

e⁻
Ag rod
Cu strip
Porous
clay wall
0.1 M AgNO₃
0.1 M CuSO₄

FIGURE 15-5

A cell with a porous clay wall connecting the solutions.

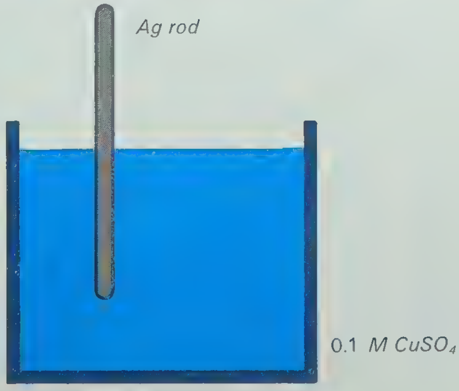

Ag rod
0.1 M CuSO₄

FIGURE 15-6

Does a chemical reaction occur? No.
$Ag(s) + Cu^{2+}(aq) \longrightarrow$ No visible reaction.

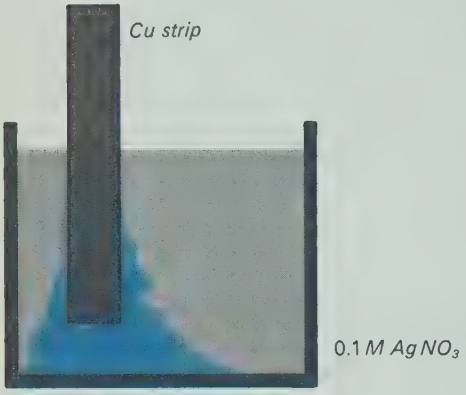


FIGURE 15-7

Does a chemical reaction occur? Yes.
$Cu(s) + 2Ag^+(aq) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$

connected with a wire. Chemical reactions take place as before. Copper dissolves at the anode; silver is deposited at the cathode.

In Figure 15-5, the salt bridge has been removed. A porous clay wall separates the two half-cells. Once again copper dissolves at the anode; silver is deposited at the cathode. What happens if we take the clay wall away and mix the solutions? Chemical reactions still occur. Two additional experiments are suggested. Does any chemical reaction take place if a silver rod is placed in a copper sulfate solution? Does any reaction occur if a copper strip is placed in a silver nitrate solution? Experiments provide answers to these questions. Figures 15-6 and 15-7 show what happens. There is no visible reaction when a silver rod is placed in a copper sulfate solution. However, the fact that silver crystals form and the solution turns blue indicates that a chemical reaction does occur when metallic copper is placed in a silver nitrate solution.

Perhaps you recognize that the chemical system described in Figure 15-7 is identical with the one studied in Experiment 7. Copper dissolved as metallic silver crystallized. The mole ratio of Cu to Ag that you found in Experiment 7 was the same as the ratio in our cell. The overall reaction is the same. It seems reasonable to explain the reaction in the beaker in the same way the reactions in the cell were explained. Of course, there is no external circuit for electrons to flow through. The electron transfer occurs as silver ions collide with the copper rod. Electrons leave the copper and react with the Ag^+ ions. Schematically this transfer can be shown as an intermediate step.

$$Cu(s) + 2\,Ag^+ \quad \boxed{Cu^{2+} - - - 2\,e^- - - - 2\,Ag^+} \longrightarrow Cu^{2+} + 2\,Ag(s)$$

Because of the presence of Cu, silver ion is reduced. Chemists say that Cu acts as a **reducing agent.** At the same time, Cu is oxidized because of the presence of Ag^+. Chemists refer to Ag^+ as the **oxidizing agent**.

Many other oxidation-reduction reactions take place in aqueous solutions. One of these was mentioned in Section 14-1 when acids were discussed.

$$Zn(s) + 2\,H^+ \longrightarrow Zn^{2+} + H_2(g)$$

Each Zn atom loses two electrons. Two H^+ ions gain electrons; molecular hydrogen forms. Zinc atoms are oxidized; hydrogen ions are reduced. This reaction can be written as two half-reactions.

$$\begin{array}{rcll} Zn(s) & \longrightarrow & Zn^{2+} + 2\,e^- & \text{oxidation} \\ 2\,e^- + 2\,H^+ & \longrightarrow & H_2(g) & \text{reduction} \\ \hline Zn(s) + 2\,H^+ & \longrightarrow & Zn^{2+} + H_2(g) & \text{net equation} \end{array}$$

Not all metals react with acids. Among the more common metals, magnesium, aluminum, zinc, iron, and nickel react with HCl solutions to form H_2. Other metals such as copper, mercury, silver, and gold do not react with HCl solutions. Apparently some metals release electrons to H^+ and others do not.

As a third oxidation-reduction example, place a strip of metallic zinc in a solution of copper nitrate. The zinc is soon coated with metallic copper and the blue color of Cu^{2+} in the solution disappears. Chemical tests show that the zinc ion, Zn^{2+}, forms and the concentration of Cu^{2+} decreases. The net equation

$$Zn(s) + Cu^{2+} \longrightarrow Zn^{2+} + Cu(s)$$

can be separated into two equations.

$$\begin{aligned} Zn(s) &\longrightarrow Zn^{2+} + 2\,e^- && \text{oxidation} \\ 2\,e^- + Cu^{2+} &\longrightarrow Cu(s) && \text{reduction} \end{aligned}$$

Zinc atoms are oxidized and copper ions are reduced. Here, copper ions *gain* electrons from zinc atoms. In Experiment 7 and in the reaction shown in Figure 15-7, copper atoms *lost* electrons to silver ions.

15-3 Competition for Electrons

The reactions that have been discussed can be viewed as competition for electrons. A state of equilibrium will be reached when this competition reaches a balance between opposing reactions. For the reaction of metallic copper with silver nitrate solution, the Cu(s) releases electrons and Ag^+ ions accept them. At equilibrium the products Cu^{2+} and Ag(s) are greatly favored.

The same sort of competition for electrons is involved in the reaction between Zn(s) and Cu^{2+}. In this system equilibrium greatly favors the products, Zn^{2+} and Cu(s). By way of contrast, compare the reaction of metallic cobalt with a nickel sulfate solution. Reaction occurs.

$$Co(s) + Ni^{2+} \longrightarrow Co^{2+} + Ni(s)$$

At equilibrium, chemical tests show that both Ni^{2+} and Co^{2+} ions are present at moderate concentrations. In this example, neither reactants nor products are greatly favored at equilibrium.

Competition for electrons in redox reactions is very similar to the competition for protons in acid-base reactions.

$$HB_1 + B_2 \;-\!\!\boxed{B_1^- \text{ - - - } H^+ \text{ - - - } B_2}\!\!\longrightarrow B_1^- + HB_2^+$$

$$M_1 + M_2^+ -\!\!\boxed{M_1^+ \text{ - - - } e^- \text{ - - - } M_2^+}\!\!\longrightarrow M_1^+ + M_2$$

The similarity suggests that a table might be developed in which metals are listed by tendency to release electrons just as earlier, acid strength was associated with the tendency to release protons (Table 14-4, page 267). We can start with the half-reactions encountered in this chapter. The equation for the reactions will be written to show the release of electrons and then arranged in order of their tendency to do so.

In the reaction between copper and silver ions, copper releases electrons to Ag^+. This experimental observation leads us to arrange the equations for the two half-reactions with copper first. Copper gives up electrons more readily than silver does.

$$\begin{aligned} Cu(s) &\longrightarrow Cu^{2+} + 2\,e^- \\ Ag(s) &\longrightarrow Ag^+ + e^- \end{aligned}$$

Another reaction discussed in Section 15-2 showed that zinc releases electrons more readily than copper does. The equation for the Zn–Zn^{2+} half-reaction can be placed at the top of the list.

$$\begin{aligned} Zn &\longrightarrow Zn^{2+} + 2\,e^- \\ Cu &\longrightarrow Cu^{2+} + 2\,e^- \\ Ag &\longrightarrow Ag^+ + \quad e^- \end{aligned}$$

This order suggests that Zn(s) will release electrons to silver ions, forming silver metal and zinc ion. It is easy to test this proposal. Place a strip of zinc metal in a solution of silver nitrate. The result confirms our expectation. The zinc dissolves and crystals of metallic silver appear.

$$Zn(s) + 2\,Ag^+ \longrightarrow Zn^{2+} + 2\,Ag(s)$$

There is one more equation that can be included in the list. It was mentioned earlier that Zn(s) dissolves in a hydrochloric acid solution but Cu(s) does not. These data suggest that the H_2–H^+ half-reaction equation should be placed below Zn–Zn^{2+} but above Cu–Cu^{2+}. Hydrogen does not release electrons as readily as zinc. Hydrogen releases electrons more readily than copper or silver.

$$\begin{aligned} Zn &\longrightarrow Zn^{2+} + 2\,e^- \\ H_2 &\longrightarrow 2\,H^+ + 2\,e^- \\ Cu &\longrightarrow Cu^{2+} + 2\,e^- \\ Ag &\longrightarrow Ag^+ + \quad e^- \end{aligned}$$

EXERCISE 15-1

From the statement that nickel reacts with H^+ to give H_2 and the additional information that zinc metal reacts readily with Ni^{2+}, decide where to place the Ni–Ni^{2+} equation in our list.

In Chapter 14, we were able to make the discussion of acids and bases quantitative by using equilibrium constants. Is there a similar way to make quantitative statements for oxidation-reduction reactions? The voltages of electrochemical cells provide such a quantitative measure.

15-4 Volts, Amperes, and Coulombs

Some of the words used in describing electrochemical cells may seem quite strange to you. Perhaps their meaning will be clear if the flow of electric current through a wire is compared to the flow of water through a pipe. Suppose that you were a fireman trying to put out a fire and that you have just hooked your hose to a fire hydrant. You would be interested in three things.

> *Is there enough water available* to put out the fire? You know it won't do you much good to put out half the fire. The total amount of water available is important.
>
> *How fast can water flow* through the pipeline to the fire hydrant? You won't be able to fight the fire very effectively if there is a large reservoir of water but such a narrow pipeline that you get only a very thin trickle of water.
>
> Finally, *how high will you be able to reach* with the water coming out of your hose? How much water pressure is there in the system? If the stream of water only reaches to the third floor of a building when the fire is on the fourth floor, you will have trouble putting the fire out.

Amount of water, its flow rate, and the water pressure are important to a fireman. The same kinds of things are important when working with electrochemical cells. We need *enough* electricity, moving with adequate *rate* at sufficiently high *pressure* to do the job at hand. Table 15-1 and Figure 15-8 compare the names of important quantities in the fireman's water system with those in a chemist's electrochemical cell.

TABLE 15-1

A Comparison of Terminology

Quantity Measured	Units Used with Water	Units Used with Electricity
Amount of flow	gallons	coulombs
Rate of flow	gallons/minute	coulombs/second (also called amperes)
Tendency to flow (pressure)	pounds/inch^2	volts

Amount of water can be expressed as a number of molecules, but a more common unit is a gallon. Amount of electricity can be expressed as a number of electrons, but a more common unit is the coulomb. A coulomb is 1.04×10^{-5} mole of electrons.

Rate of flow is amount divided by time. Gallons per minute for water and coulombs per second for electricity are often used to indicate rate of flow. One coulomb per second is also called an **ampere.** A circuit through which one coulomb is passing per second is said to be carrying a current of one ampere. In Section 15-10, the amount and rate of flow will be discussed further.

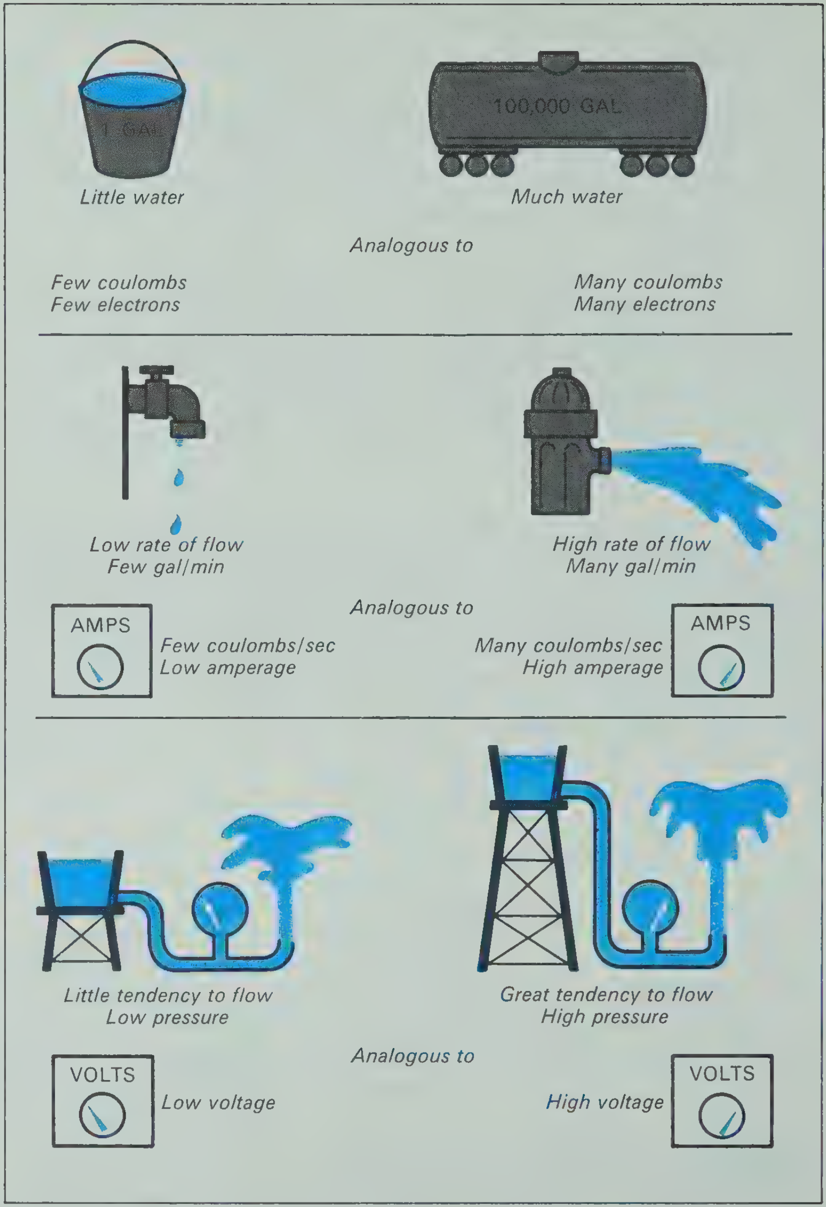

1 GAL
100,000 GAL
Little water
Much water
Analogous to
Few coulombs
Few electrons
Many coulombs
Many electrons
Low rate of flow
Few gal/min
High rate of flow
Many gal/min
Analogous to
AMPS
Few coulombs/sec
Low amperage
Many coulombs/sec
High amperage
AMPS
Little tendency to flow
Low pressure
Great tendency to flow
High pressure
Analogous to
VOLTS
Low voltage
High voltage
VOLTS

FIGURE 15-8

Comparison of terms used for water and electricity.

Electrical pressure is expressed in volts. Voltage is just one of the many ways to talk about potential energy. The electrical voltage corresponds directly to the water pressure in our story of the fireman. A high voltage means that electrons are in a high energy state. When the switch is closed in an electric circuit, electrons move through the circuit. They may operate a motor or perhaps light a light bulb. Like water flowing downhill, electrons spontaneously move from a position of high potential energy to one of low potential energy. The voltage of a cell measures its tendency to do electrical work. Different cells show different voltages.

15-5 The Voltage of an Electrochemical Cell and the Tendency to Release Electrons

We would like to measure the contribution each half-reaction makes to the cell voltage. The voltage for a particular cell may be considered as having two parts, the first characteristic of one half-reaction and the second part characteristic of the other half-reaction. Chemists call these two contributions to the cell voltage "half-cell potentials," a term that emphasizes the relation between voltage and potential energy. Half-cell potentials are symbolized E. Since the voltage of a cell depends on concentration and temperature, chemists have agreed to use 25°C as the reference temperature. For ionic solutions, the reference concentration is 1 M. For gases, a pressure of one atmosphere is chosen as the standard pressure. The symbol E° is used to indicate that measurements have been carried out at the reference temperature, pressure, and concentration.

There is a close parallel between the half-reaction view of redox reactions and the Bronsted concept of acids and bases. To establish a table of acid strengths, the tendency of an acid to donate protons to a reference base, H_2O, was determined. In redox reactions, chemists have agreed to use the $H_2(g)–H^+$ half-reaction as the reference system. The value 0.00 volt for this half-reaction is an arbitrary assignment. It is convenient to measure the tendency for a substance M to donate an electron to H^+.

FIGURE 15-9A

The $Zn–Zn^{2+}$ half-cell compared to the hydrogen reference half-cell.

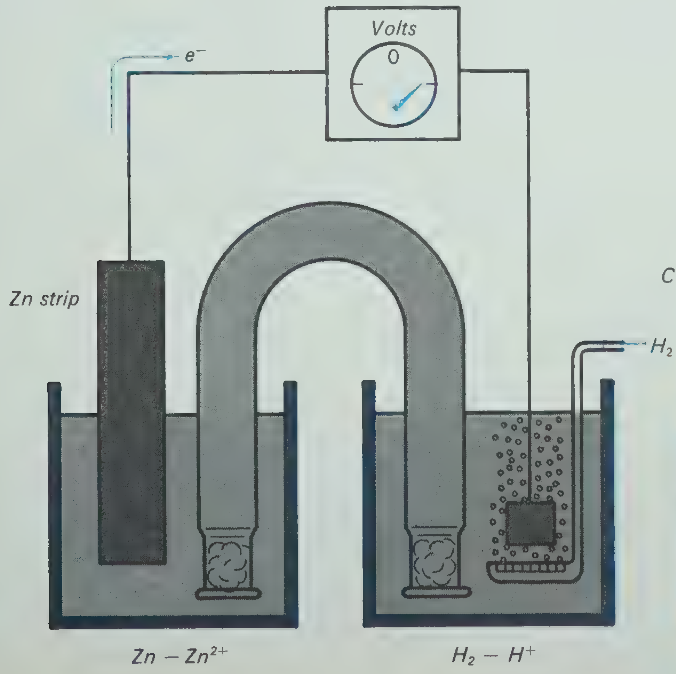
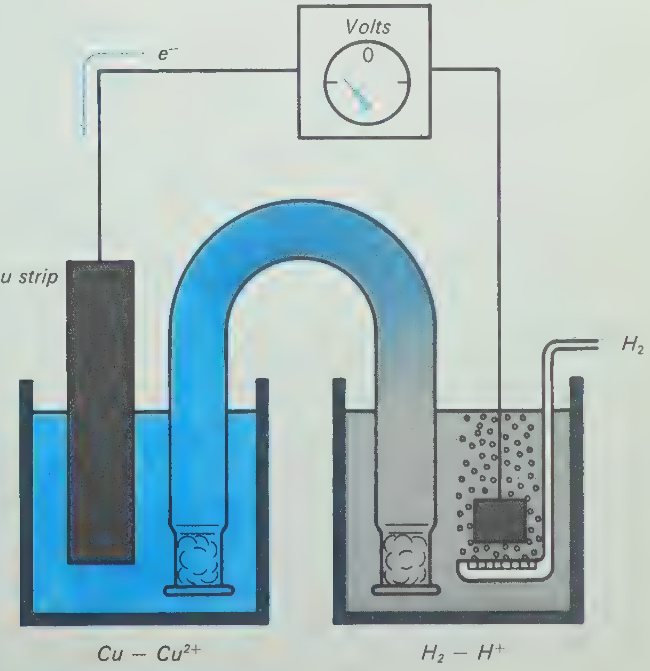


FIGURE 15-9B

The $Cu–Cu^{2+}$ half-cell compared to the hydrogen reference half-cell.



Electrochemical cells can be constructed in which one half-cell is always the reference system, $H_2(g)–H^+$. The other half-cell can be changed. Figure 15-9 shows two examples, with the reference half-cell on the right side of each diagram. The first drawing (A) represents the cell made from the $Zn–Zn^{2+}$ and $H_2–H^+$ half-cells. Experiments show that zinc dissolves and hydrogen gas forms when this cell operates. The equation for the overall reaction is:

$$Zn(s) + 2\,H^+ \longrightarrow Zn^{2+} + H_2(g)$$

The voltmeter shows a reading of 0.76 volt for this combination of half-cells. Since chemists have chosen the $H_2–H^+$ half-reaction for the reference system, then the voltage of the entire cell can be assigned to the $Zn–Zn^{2+}$ half-reaction. The positive sign, $E° = +0.76$ volt, indicates that Zn has *greater* tendency to release electrons than does H_2.

$$Zn \longrightarrow Zn^{2+} + 2\,e^- \qquad E° = +0.76 \text{ volt}$$

The second electrochemical cell in Figure 15-9 is made from the two half-cells, $Cu–Cu^{2+}$ and $H_2–H^+$. Experiments show that the overall reaction for this system is:

$$Cu^{2+} + H_2(g) \longrightarrow Cu(s) + 2\,H^+$$

The voltmeter indicates a value of 0.34 volt. As before this voltage can be assigned to the $Cu–Cu^{2+}$ half-reaction.

There is one striking difference between the two cells in Figure 15-9. The voltmeter needle moves one way for the zinc-hydrogen cell. For the copper-hydrogen cell the voltmeter needle moves the other direction which suggests that hydrogen molecules have *more* tendency to donate electrons than copper atoms do. The $H_2–H^+$ electron donating tendency is represented by 0.00 volt. We indicate that copper has even less tendency to give up electrons by using a negative sign with its voltage. Notice how the electron releasing tendency for the three half-reactions is indicated by the sign of $E°$.

$$\begin{aligned} Zn(s) &\longrightarrow Zn^{2+} + 2\,e^- &\qquad E° &= +0.76 \text{ volt} \\ H_2(g) &\longrightarrow 2\,H^+ + 2\,e^- &\qquad E° &= 0.00 \text{ volt} \\ Cu(s) &\longrightarrow Cu^{2+} + 2\,e^- &\qquad E° &= -0.34 \text{ volt} \end{aligned}$$

Chemists have determined a large number of half-cell voltages. The magnitude of the voltage is a quantitative measure of the tendency for that half-reaction to release electrons in comparison to the $H_2–H^+$ half-reaction. If the sign is *positive*, the half-reaction has a *greater* tendency to release electrons than does H_2. If the sign is *negative*, the half-reaction has *less* tendency to release electrons than does H_2.

TABLE 15-2

Standard Oxidation Potentials for Some Half-Reactions

Very strong reducing agents

Reducing strength increases

Reduced State		Oxidized State	E° (Volts)
Al	$\longrightarrow$	$3e^- + Al^{3+}$	+1.66
Zn	$\longrightarrow$	$2e^- + Zn^{2+}$	+0.76
Fe	$\longrightarrow$	$2e^- + Fe^{2+}$	+0.44
$Pb + SO_4^{2-}$	$\longrightarrow$	$2e^- + PbSO_4$	+0.36
Co	$\longrightarrow$	$2e^- + Co^{2+}$	+0.28
Ni	$\longrightarrow$	$2e^- + Ni^{2+}$	+0.25
H_2	$\longrightarrow$	$2e^- + 2H^+$	+0.00
Cu	$\longrightarrow$	$2e^- + Cu^{2+}$	−0.34
$2I^-$	$\longrightarrow$	$2e^- + I_2$	−0.53
Fe^{2+}	$\longrightarrow$	$e^- + Fe^{3+}$	−0.77
Ag	$\longrightarrow$	$e^- + Ag^+$	−0.80
$NO + 2H_2O$	$\longrightarrow$	$3e^- + 4H^+ + NO_3^-$	−0.96
$2Br^-$	$\longrightarrow$	$2e^- + Br_2$	−1.06
$2H_2O$	$\longrightarrow$	$4e^- + 4H^+ + O_2$	−1.23
$2Cl^-$	$\longrightarrow$	$2e^- + Cl_2$	−1.36
$Mn^{2+} + 4H_2O$	$\longrightarrow$	$5e^- + 8H^+ + MnO_4^-$	−1.52
$PbSO_4 + 2H_2O$	$\longrightarrow$	$2e^- + 4H^+ + SO_4^{2-} + PbO_2$	−1.68
$2F^-$	$\longrightarrow$	$2e^- + F_2$	−2.87

Oxidizing strength increases

Very strong oxidizing agents

In Table 14-4, page 267, acids are arranged in order of their tendency to donate protons to the reference base H_2O. Table 15-2 contains a similar arrangement for reducing agents, showing their tendency to donate electrons to the reference oxidizing agent H^+. A more complete list is given in Appendix 4.

15-6 Predicting Redox Reactions

Chemists use half-cell potentials to predict whether an oxidation-reduction reaction can occur. Here are a few examples.

Will iron dissolve in a solution that is 1 *M* in Ni^{2+}? We perform an experiment and find that it does. How can this observation be related to the tendency to donate electrons? The two half-reactions which must be considered appear in Table 15-2.

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad E_1^\circ = +0.44 \text{ volt}$$
$$Ni \longrightarrow Ni^{2+} + 2e^- \qquad E_2^\circ = +0.25 \text{ volt}$$

From E° values it can be concluded that iron has a greater tendency to donate electrons than does nickel. This suggests that iron can transfer electrons to the ion, Ni^{2+}. Reversing the second equation changes the sign for E_2°. We can add the two half-reactions and also the two E° values.

$$\begin{array}{llll} \mathrm{Fe} & \longrightarrow \mathrm{Fe^{2+}} + 2\,e^- & & E_1^\circ = +0.44 \text{ volt} \\ 2\,e^- + \mathrm{Ni^{2+}} & \longrightarrow \mathrm{Ni} & & E_2^\circ = -0.25 \text{ volt} \\ \hline \mathrm{Fe} + \mathrm{Ni^{2+}} & \longrightarrow \mathrm{Ni} + \mathrm{Fe^{2+}} & & \text{net } E^\circ = +0.19 \text{ volt} \end{array}$$

Chemical reaction occurs, with metallic iron being oxidized to Fe^{2+} and metallic nickel forming by reduction of Ni^{2+}. The positive sign for the net voltage means that the products will be present in higher concentrations at equilibrium than will the reactants.

Here is another example. A number of metals are oxidized by 1 *M* HCl to produce hydrogen gas. When this experiment is carried out with silver as the metal, there is no appreciable reaction. However, silver metal is readily oxidized by 1 *M* HNO_3. The information in Table 15-2 helps us to understand these reactions.

$$\begin{array}{lll} \mathrm{H_2} \longrightarrow 2\,\mathrm{H^+} + 2\,e^- & & E_1^\circ = 0.00 \text{ volt} \\ 2\,\mathrm{Ag} \longrightarrow 2\,\mathrm{Ag^+} + 2\,e^- & & E_2^\circ = -0.80 \text{ volt} \end{array}$$

To solve the problem we have posed, these half-reactions must be combined so that Ag and H^+ are reactants. This is achieved by writing the first as chemical reduction instead of oxidation.

$$\begin{array}{lll} 2\,e^- + 2\,\mathrm{H^+} \longrightarrow \mathrm{H_2} & & E_1^\circ = 0.00 \text{ volt} \\ 2\,\mathrm{Ag} \longrightarrow 2\,\mathrm{Ag^+} + 2\,e^- & & E_2^\circ = -0.80 \text{ volt} \\ \hline 2\,\mathrm{Ag} + 2\,\mathrm{H^+} \longrightarrow 2\,\mathrm{Ag^+} + \mathrm{H_2} & & \text{net } E^\circ = -0.80 \text{ volt} \end{array}$$

From a simple experiment we know that Ag does not dissolve in 1 *M* H^+. The E° for the net reaction is negative. These two ideas are always found together.

> A *negative voltage* for a reaction means that at equilibrium, the concentrations of reactants are higher than the concentrations of products.

Notice that the E° value for the Ag–Ag^+ half-reaction was not doubled even though the equation has been multiplied by two. The voltage of a cell does not depend on how many moles take part in a reaction. Voltage is a measure of electrical pressure. The pressure caused by water does not depend on how much water is present. Pressure depends on potential energy which is determined by the height of the water. The voltage caused by a cell does not depend on how much matter is present. Voltage depends on potential energy which is determined by the bonding arrangement in the chemicals. Changing the number of moles does not change the voltage for an electrochemical reaction.

EXERCISE 15-2

Calculate the potential expected for the following combinations of half-reactions. Assume all ions are 1 *M*.

(a) $Co + Fe^{3+}$ gives $Co^{2+} + Fe^{2+}$

(b) $H_2 + Cl_2$ gives $H^+ + Cl^-$

(c) $I^- + MnO_4^-$ in acid solution gives $I_2 + Mn^{2+}$

Answer: +0.99 volt

(d) Will $Ag + Cl^-$ produce $Ag^+ + Cl_2$?

To understand the reaction of silver with nitric acid, it seems reasonable to focus attention on the nitrate ion. The example above showed that H^+ is not effective. The equations are

$$\begin{array}{rll} 3\,Ag \longrightarrow 3\,Ag^+ + 3\,e^- & & E_1^\circ = -0.80 \text{ volt} \\ 3\,e^- + 4\,H^+ + NO_3^- \longrightarrow NO + 2\,H_2O & & E_2^\circ = +0.96 \text{ volt} \\ \hline 4\,H^+ + 3\,Ag + NO_3^- \longrightarrow 3\,Ag^+ + NO + 2\,H_2O & & \text{net } E^\circ = +0.16 \text{ volt} \end{array}$$

Experiments show that silver dissolves in 1 *M* HNO_3. The E° value for the net reaction is positive. These two ideas are always found together.

> The *positive voltage* for a reaction means that at equilibrium, the concentrations of products are higher than the concentrations of reactants.

In Chapter 14, page 268, a useful regularity was suggested to help predict whether an acid-base reaction favored reactants or products. A similar regularity can be proposed for redox reactions. In Table 15-2, the strong reducing agents are at the top left side of the half-reaction list. Aluminum is the strongest reducing agent shown. The strong oxidizing agents are at the bottom right side of the half-reaction list. Fluorine is the strongest oxidizing agent shown.

> A substance in the left column in Table 15-2 tends to react spontaneously with any substance in the right column that is *lower* in the table.

Qualitative predictions about redox reactions can be made using this regularity. For example, we expect Cu(s) to be oxidized to Cu^{2+} by Br_2 or HNO_3, but Cu(s) would not react with Fe^{2+} or Zn^{2+}.

EXERCISE 15-3

Use E° values in Table 15-2 to predict whether cobalt metal will dissolve in 1 *M* HCl solution. Then predict whether cobalt metal will dissolve in 1 *M* zinc sulfate solution.

EXERCISE 15-4

Use Table 15-2 to decide which substances in the following list tend to oxidize bromide ion, Br^-.

Cl_2, H^+, Ni^{2+}, HNO_3, O_2

EXERCISE 15-5

Use Table 15-2 to decide which substances in the following list tend to reduce bromine, Br_2.

$$Cl^-, \; H_2, \; Ni, \; Fe^{2+}$$

SPONTANEOUS REDOX REACTIONS

15-7 Storage Batteries and Electrochemical Cells

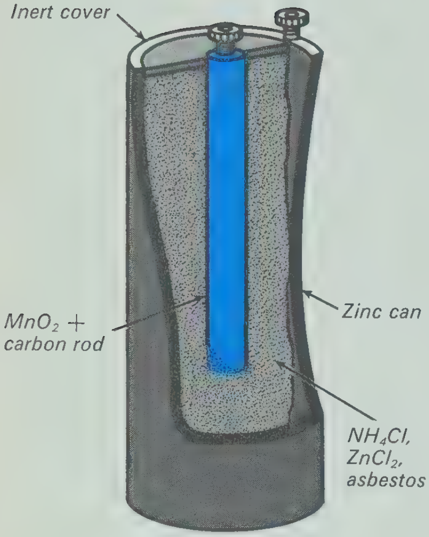


FIGURE 15-10

A cutaway view of a dry cell.

Electrochemical cells have very great practical importance. They can supply energy at any time we want to use it. Two familiar examples are the cells used in flashlights and the lead storage battery used in starting some automobiles. Recently there has been renewed interest in developing electrochemical cells that might replace the internal combustion engine in an automobile.

The most common flashlight cell is shown in Figure 15-10. A zinc container, the anode, is filled with a paste of ammonium chloride, zinc chloride, water, and an inert filler such as asbestos. This medium acts as a salt bridge. The central electrode, the cathode, is a mixture of carbon and manganese dioxide, MnO_2. The chemical reactions taking place in this cell depend on the amount of electric current drawn. When small currents are involved, these reactions probably occur.

$$\begin{array}{lr}
\text{At the anode:} & Zn + 4\,NH_3 \longrightarrow Zn(NH_3)_4^{2+} + 2\,e^- \\
\text{At the cathode:} & 2\,MnO_2 + 2\,NH_4^+ + 2\,e^- \longrightarrow Mn_2O_3 + 2\,NH_3 + H_2O
\end{array}$$

The lead storage battery contains several of the cells shown schematically in Figure 15-11. The reactions in this electrochemical cell can be represented in this manner.

$$\begin{array}{lrl}
\text{At the anode:} & Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2\,e^- & E_1^\circ = +0.36 \text{ volt} \\
\text{At the cathode:} & PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O & E_2^\circ = +1.68 \text{ volts} \\
\hline
\text{Net reaction:} & Pb + PbO_2 + 4\,H^+ + 2\,SO_4^{2-} \longrightarrow 2\,PbSO_4 + 2\,H_2O & E^\circ = +2.04 \text{ volts}
\end{array}$$

The net reaction above shows that H_2SO_4 is consumed as the battery is discharged. In addition, H_2O is formed. Over a period of time, the electrolyte becomes more dilute. Measuring the density of the sulfuric acid electrolyte provides a simple way to know when your battery should be recharged. High density for the electrolyte means the sulfuric acid concentration is large; low density means the sulfuric acid concentration is low. In areas where the winter temperatures go below 0°C, it is important to keep a car battery charged. Concentrated solutions freeze at lower temperatures than dilute ones do.

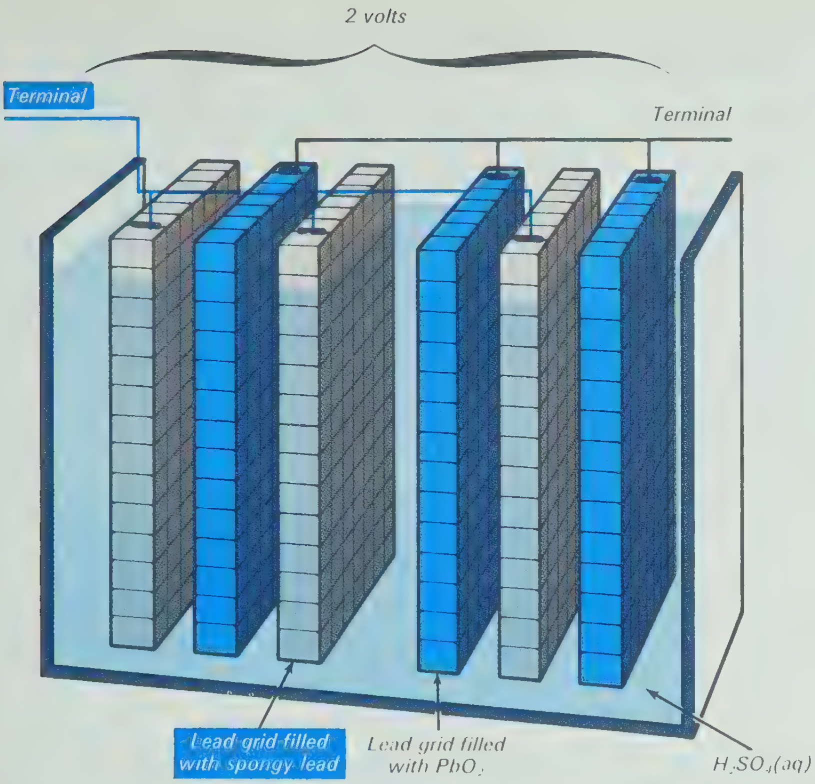

2 volts
Terminal
Terminal
Lead grid filled with spongy lead
Lead grid filled with PbO_2
$H_2SO_4(aq)$

FIGURE 15-11

View into a single lead storage cell.

Several other cells are used for special purposes. The AgO–Cd cell has been used in satellites. This cell can produce a large supply of electrical power and yet it can be made quite small. The electrolyte solution contains KOH. The equations for the half-reactions are:

$$Cd + 2\,OH^- \longrightarrow Cd(OH)_2 + 2\,e^- \qquad E_1^\circ = +0.81 \text{ volt}$$

$$2\,AgO + H_2O + 2\,e^- \longrightarrow Ag_2O + 2\,OH^- \qquad E_2^\circ = +0.57 \text{ volt}$$

Miniature batteries are used in watches, movie cameras, and hearing aids to give self-contained power. These batteries often are made of HgO–Zn or Ag_2O–Zn. As a last example of cells, we mention fuel cells. These are systems that convert the potential energy of chemicals like H_2 or CH_4 directly to electrical energy. Such cells can operate at about 70% efficiency. The usual process of burning a fuel and using the heat energy to form steam for driving turbines is about 20% efficient. A schematic drawing for a CH_4–O_2 fuel cell is shown in Figure 15-12. The electrode reactions can be represented with these equations.

$$\begin{array}{lrcl|l}
\text{Anode:} & CH_4 + 10\,OH^- & \longrightarrow & CO_3^{2-} + 7\,H_2O + 8\,e^- & E_1^\circ = -0.17 \text{ volt} \\
\text{Cathode:} & 2\,O_2 + 4\,H_2O + 8\,e^- & \longrightarrow & 8\,OH^- & E_2^\circ = +0.40 \text{ volt} \\
\hline
\text{Net reaction:} & 2\,O_2 + CH_4 + 2\,OH^- & \longrightarrow & CO_3^{2-} + 3\,H_2O & E^\circ = +0.23 \text{ volt}
\end{array}$$

This reaction is very slow at room temperature. Suitable catalysts are necessary to accelerate the electrode reactions.

15-8 Corrosion of Iron, an Undesirable Redox Reaction

All of us know that an object made of iron soon shows signs of rusting if it is left outside, exposed to the air. Rusting or corrosion of iron is a serious economic problem. In fact, one out of every four men in the steel industry works to replace the iron lost by rusting! This shows how important control of corrosion is. What is the chemical nature of rusting and how can it be controlled? The observed facts are:

H_2O and O_2 are necessary.
H^+ speeds up the reaction.
Some metals such as zinc and magnesium retard rusting.
Corrosion occurs rapidly where there are the greatest strains in the object.

How can these observations be interpreted? The most promising mechanism seems to require a series of steps that correspond to the operation of an electrochemical cell.

(1) Iron acts as an anode to release two electrons, forming Fe^{2+}. This process seems to start most often at a strain point in the metal.
(2) Electrons move through the external circuit (in this case, the iron bar itself). Hydrogen ions, H^+, in water on the surface of the bar accept the electrons. Neutral H atoms form.
(3) Oxygen in air reacts rapidly with H to form H_2O.
(4) Ferrous ions are oxidized by oxygen, in the presence of water, to form rust.
(5) To complete the electric circuit, electric charge must be carried back to the initial point of corrosion. A film of moisture on the iron bar serves as an effective salt bridge.

The comparison between the steps in corrosion and an electrochemical cell suggests a number of ways to minimize corrosion. If we interrupt the circuit at any point, electric charge cannot move from the anode to the cathode and back to the anode. Excluding O_2 would interfere with step 3; excluding H_2O would prevent steps 2, 4, and 5. The most effective way to exclude O_2 and H_2O is to cover the iron bar with grease, paint, or a metal like tin which is a weaker reducing agent than iron. Any break in the tin covering, however, gives rise to faster rusting than before. A "tin can" which is tin-covered steel rusts rapidly after it starts to corrode.

A much better way to prevent corrosion of iron involves bringing a stronger reducing agent than iron into the system. A metal such as zinc or magnesium in close contact with iron becomes the anode, forcing iron to act as the cathode. The zinc or magnesium piece is oxidized, releasing electrons. The iron bar does not corrode. Ship

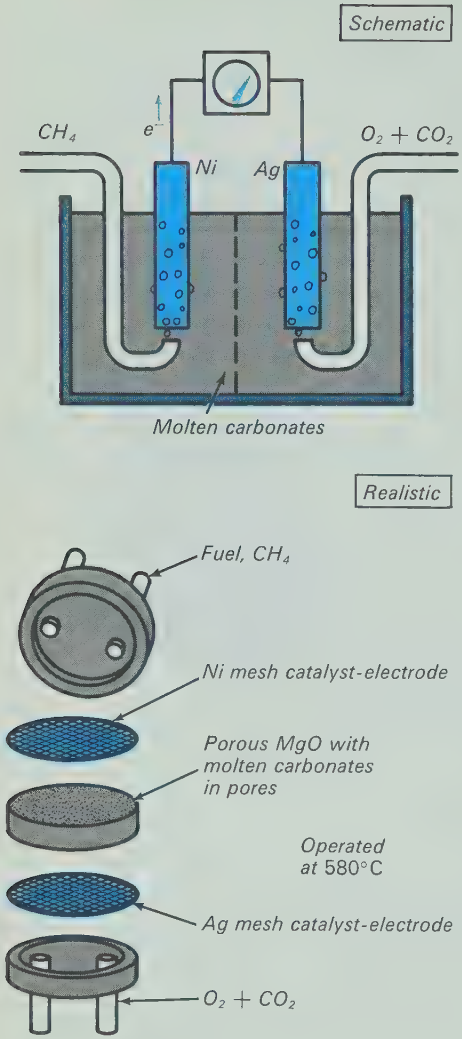

Schematic
e⁻
CH₄
O₂ + CO₂
Ni
Ag
Molten carbonates
Realistic
Fuel, CH₄
Ni mesh catalyst-electrode
Porous MgO with molten carbonates in pores
Operated at 580°C
Ag mesh catalyst-electrode
O₂ + CO₂

FIGURE 15-12

Two versions of a methane-O_2 fuel cell.

hulls are protected in this fashion. Large blocks of magnesium metal are bolted to the steel hulls. The magnesium oxidizes largely preventing loss of iron from the hull.

NONSPONTANEOUS REDOX REACTIONS

15-9 The Electrolytic Process

This chapter has been concerned with redox reactions that proceed spontaneously. But the same ideas can be applied to reactions that are forced to take place, against their natural tendency. We do this by supplying energy with an externally applied electric current. Such a process is termed **electrolysis.** In Chapter 3, page 43, electrolysis of water was discussed. The parts of a suitable circuit can be listed.

(1) Two carbon rods to serve as electrodes.
(2) A solution of sulfuric acid, 1 *M* in H^+.
(3) An ammeter to show current flow in the system.
(4) A voltmeter to indicate the voltage applied to the cell.
(5) The battery to provide any voltage we want from 0.0 volt up to 2.0 volts.

The voltage is gradually increased. At low voltages there is no current flow through the circuit and there is no visible change in the solution. But when the voltmeter reads 1.23 volts, bubbles of gas begin to form at each electrode. The ammeter indicates that electric current flows through the circuit. As the voltage is increased further, the current increases. The evolution of gas at each electrode also increases. Chemical tests show that the gas formed at the cathode is H_2 and the gas formed at the anode is O_2. The equation for the reaction is

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

Since this is an oxidation-reduction reaction, we can write equations for the two half-reactions

$$\begin{array}{lll} & 2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^- & E_1^\circ = -1.23 \text{ volts} \\ & 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2 & E_2^\circ = 0.00 \text{ volt} \\ \hline \text{Net equation} & 2\,H_2O \longrightarrow 2\,H_2 + O_2 & E^\circ = -1.23 \text{ volts} \end{array}$$

The negative voltage tells us that the reaction is not spontaneous. No electrode reactions can take place until the voltage from the battery in the external circuit reaches at least 1.23 volts. That much electrical pressure is necessary to oppose the voltage that the electrochemical cell can generate. In practice, more than 1.23 volts must be applied to get current flow. The reasons are too complex to discuss here.

An important electrolytic method converts 98–99% pure copper into 99.9+% copper. Copper is second only to silver as a conductor of electricity and is widely used in electrical circuits. However, small amounts of impurities reduce the conductivity of copper. An electrolytic cell can be used to purify copper. Figure 15-13 shows this process in use. The impure copper is made the anode and a thin sheet of very pure copper serves as the cathode. The solution in the cells contains copper sulfate. As soon as any voltage is applied to the cells, current flows. The copper anode is oxidized to Cu^{2+} ions. Copper deposits on the cathode as Cu^{2+} ions are reduced. The equations for the electrode reactions show what happens during this electrolysis.

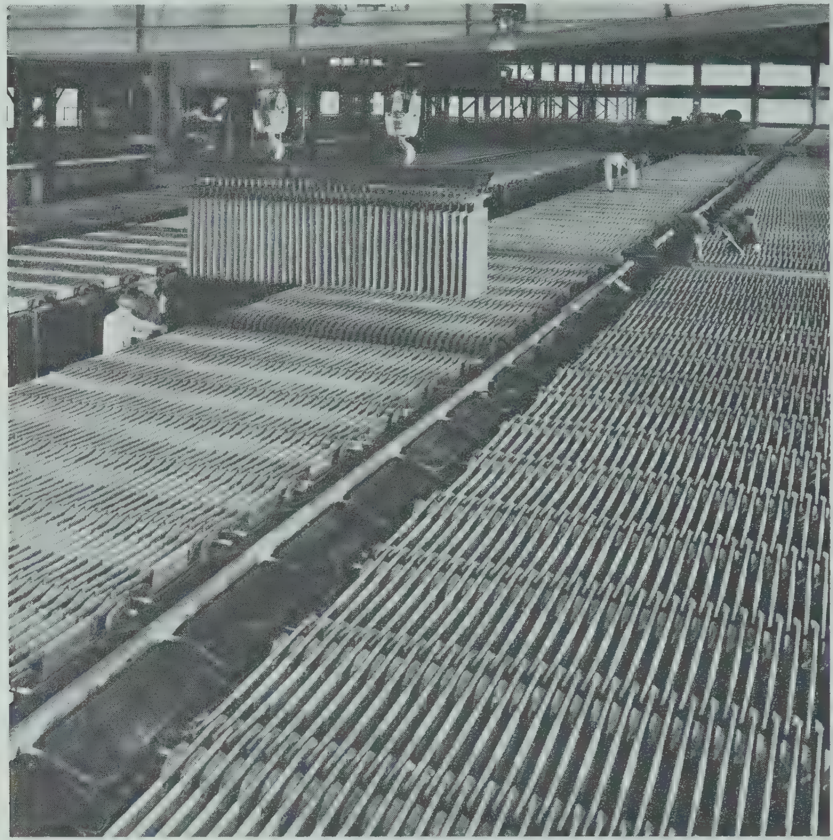


FIGURE 15-13

Electrolysis cells for purifying copper. Utah Copper Division, Kennecott Copper Corporation.

$$\begin{array}{rcll}
\text{Cu (anode)} & \longrightarrow & \text{Cu}^{2+} + 2\,e^- & E_1^\circ = -0.34 \text{ volt} \\
2\,e^- + \text{Cu}^{2+} & \longrightarrow & \text{Cu (cathode)} & E_2^\circ = +0.34 \text{ volt} \\
\hline
\text{Cu (anode)} & \longrightarrow & \text{Cu (cathode)} & E^\circ = 0.00 \text{ volt}
\end{array}$$

Here is an interesting situation! Apparently the only change during this electrolysis is the transport of copper from the anode to the cathode. Common impurities in copper are iron and silver. The first is an element which is more easily oxidized than copper and the second is an element which is less readily oxidized than copper. The equations and E° values for the half-reactions of these three elements are

$$\begin{array}{lll}
\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\,e^- & & E^\circ = +0.44 \text{ volt} \\
\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\,e^- & & E^\circ = -0.34 \text{ volt} \\
\text{Ag} \longrightarrow \text{Ag}^{+} + e^- & & E^\circ = -0.80 \text{ volt}
\end{array}$$

If the voltage is controlled, only iron and copper are oxidized at the anode. The silver is not oxidized. It drops to the bottom of the electrolytic cell and is recovered by other means. At the cathode, copper is more readily reduced and iron stays in solution. Only copper, with very high purity, plates out on the cathode.

EXERCISE 15-6

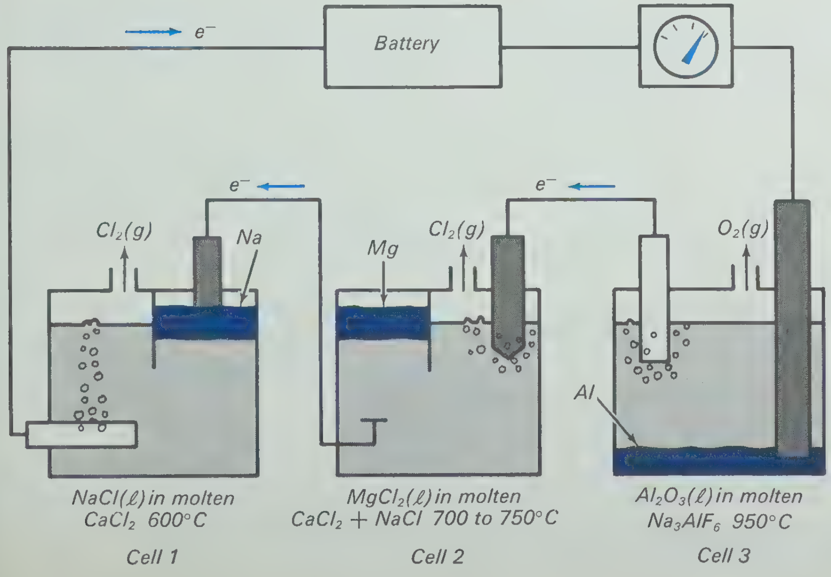
The electrolysis of fused NaCl produces sodium metal at the cathode and chlorine gas at the anode. Write equations for the two half-reactions that occur in this electrolysis.

A number of other substances are made commercially by electrolysis. Some of them are illustrated in the next section as part of the study of how much electricity is needed to produce a given mass of material.

15-10 Quantitative Relations in Electrolysis

Michael Faraday was the first chemist who tried to explain electrolysis. His experiments offered support for Dalton's Atomic Theory. Electricity, like atoms, seemed to come only in packages. Today electrolysis can be treated in a quantitative fashion in terms of half-reactions and their $E°$ values.

Figure 15-14 shows three electrolytic systems of great industrial importance. These cells are connected. When the switch is closed, electrons flow in the circuit. The current entering the cell on the right will be the same as the current leaving the cell on the left. The same number of electrons move through each cell per unit time. The total electric charge carried through this circuit can be calculated.



$NaCl(\ell)$ in molten $CaCl_2$ 600°C
Cell 1

$MgCl_2(\ell)$ in molten $CaCl_2 + NaCl$ 700 to 750°C
Cell 2

$Al_2O_3(\ell)$ in molten Na_3AlF_6 950°C
Cell 3

FIGURE 15-14

Three electrolytic processes used in industry.

Millikan's oil drop experiment (Section 6-5, page 90) showed that the charge on the electron equals 1.6×10^{-19} coulomb. One mole of electrons would carry a total charge of

$$\left(1.6 \times 10^{-19} \frac{\text{coulomb}}{\text{electron}}\right)\left(6.0 \times 10^{23} \frac{\text{electrons}}{\text{mole}}\right) = 9.6 \times 10^{4} \frac{\text{coulombs}}{\text{mole}}$$

More precise measurements lead to a value of 96,454 coulombs per mole of electrons. This number is referred to as "one Faraday" in recognition of Michael Faraday's contributions to electrochemistry. The equations for the half-reactions indicate what is taking place in each cell.

	Cathode reactions	Anode reactions
Cell 1	$Na^+ + e^- \longrightarrow Na(s)$	$Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$
Cell 2	$\frac{1}{2} Mg^{2+} + e^- \longrightarrow \frac{1}{2} Mg(s)$	$Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$
Cell 3	$\frac{1}{3} Al^{3+} + e^- \longrightarrow \frac{1}{3} Al(s)$	$\frac{1}{2} H_2O \longrightarrow \frac{1}{4} O_2 + e^- + H^+$

When 9.6×10^4 coulombs of electricity pass through this circuit, one mole of electrons moves through each of the three cells. The net chemical reactions produce

Cell 1	1 mole Na plus $\frac{1}{2}$ mole Cl_2
Cell 2	$\frac{1}{2}$ mole Mg plus $\frac{1}{2}$ mole Cl_2
Cell 3	$\frac{1}{3}$ mole Al plus $\frac{1}{4}$ mole O_2

The total number of coulombs moving through an electrical circuit measures the total flow of electricity. The rate of flow, or the current passing a point, is specified by coulombs per second. A rate of one coulomb per second is called one **ampere.**

$$\text{Amperes} = \text{coulombs/second}$$

Suppose a constant current of 2.0 amperes flows through each of the three electrolytic cells for 10 hours. The number of coulombs can be calculated:

$$\begin{aligned}\text{Coulombs} &= \text{amperes} \times \text{seconds}\\ &= 2.0 \text{ amp} \times 10 \text{ hr} \times 60 \frac{\text{min}}{\text{hr}} \times 60 \frac{\text{sec}}{\text{min}}\\ &= 7.2 \times 10^4 \text{ amp·sec}\end{aligned}$$

$$\begin{aligned}\text{Moles of electrons} &= \frac{\text{Number of coulombs}}{9.6 \times 10^4 \text{ coulombs/mole}}\\ &= \frac{7.2 \times 10^4}{9.6 \times 10^4}\\ &= 0.75 \text{ mole}\end{aligned}$$

Looking at the electrode reactions given above, the mass of each product can be calculated.

Cell 1

$$\text{grams Na} = 0.75 \text{ mole electrons} \times \frac{1 \text{ mole Na}}{\text{mole electrons}} \times \frac{23 \text{ g}}{\text{mole Na}} = 17 \text{ g}$$

$$\text{grams Cl}_2 = 0.75 \text{ mole electrons} \times \frac{\tfrac{1}{2} \text{ mole Cl}_2}{\text{mole electrons}} \times \frac{71 \text{ g}}{\text{mole Cl}_2} = 27 \text{ g}$$

Cell 2

$$\text{grams Mg} = 0.75 \text{ mole electrons} \times \frac{\tfrac{1}{2} \text{ mole Mg}}{\text{mole electrons}} \times \frac{24 \text{ g}}{\text{mole Mg}} = 9.0 \text{ g}$$

$$\text{grams Cl}_2 = 0.75 \text{ mole electrons} \times \frac{\tfrac{1}{2} \text{ mole Cl}_2}{\text{mole electrons}} \times \frac{71 \text{ g}}{\text{mole Cl}_2} = 27 \text{ g}$$

Cell 3

$$\text{grams Al} = 0.75 \text{ mole electrons} \times \frac{\tfrac{1}{3} \text{ mole Al}}{\text{mole electrons}} \times \frac{27 \text{ g}}{\text{mole Al}} = 6.8 \text{ g}$$

$$\text{grams O}_2 = 0.75 \text{ mole electrons} \times \frac{\tfrac{1}{4} \text{ mole O}_2}{\text{mole electrons}} \times \frac{32 \text{ g}}{\text{mole O}_2} = 6.0 \text{ g}$$

15-11 Balancing Oxidation-Reduction Equations

A balanced equation shows that mass and electric charge are conserved in a chemical reaction. More important to the chemist, the mole ratios for reactants and products are given by the coefficients in the balanced equation. For many reactions, a bit of trial and error quickly leads to the assignment of the proper coefficients. Sometimes oxidation-reduction reactions are not readily balanced by this approach. There are systematic ways to balance redox equations. We shall discuss three methods.

Method I Balance by Inspection

In Experiment 2, you observed the reaction between metallic aluminum and cupric chloride solution. Although several chemical reactions were occurring simultaneously, the principal one was the formation of copper metal as aluminum dissolved. It is not difficult to balance the equation for this reaction. It can be done by inspection. Here are the steps.

1. Write reactants and products.

$$\text{Al} + \text{Cu}^{2+} \longrightarrow \text{Al}^{3+} + \text{Cu}$$

(Atoms balanced; charge **not** balanced)

2. Balance electric charge.

$$\text{Al} + 3\,\text{Cu}^{2+} \longrightarrow 2\,\text{Al}^{3+} + \text{Cu}$$

(Charge balanced; atoms **not** balanced)

3. Balance atoms.

$$2\,\text{Al} + 3\,\text{Cu}^{2+} \longrightarrow 2\,\text{Al}^{3+} + 3\,\text{Cu}$$

(Charge balanced; atoms balanced)

The equation is now balanced: two moles of aluminum metal will reduce three moles of cupric ion.

EXERCISE 15-7

Write balanced equations for these redox reactions by inspection.

	reactants		products
(a)	$Zn + Ag^+$	$\longrightarrow$	$Ag + Zn^{2+}$
(b)	$Cr^{2+} + I_2$	$\longrightarrow$	$I^- + Cr^{3+}$
(c)	$Ti + Fe_2O_3$	$\longrightarrow$	$TiO_2 + Fe$

Method II Use the Table of Half-Reactions

In Experiment 24, you observed that ferrous ions reacted with permanganate ions in acid solution. It is too laborious to balance the equation for this reaction by inspection, particularly since there is another, much easier, way to balance it. First write the reactants and products.

$$Fe^{2+} + MnO_4{}^- \longrightarrow Mn^{2+} + Fe^{3+}$$

Then look in the table of oxidation potentials, Appendix 4, for the two half-reactions containing these substances

$$\begin{aligned} Fe^{2+} &\longrightarrow Fe^{3+} + e^- \\ 5\,e^- + 8\,H^+ + MnO_4{}^- &\longrightarrow Mn^{2+} + 4\,H_2O \end{aligned}$$

There must be the same number of electrons in each half-reaction equation since electric charge does not build up in a redox system. Multiplying the first equation by five provides the electrons that permanganate gains.

$$\begin{aligned} 5\,Fe^{2+} &\longrightarrow 5\,Fe^{3+} + 5\,e^- \\ 5\,e^- + 8\,H^+ + MnO_4{}^- &\longrightarrow Mn^{2+} + 4\,H_2O \\ \hline 8\,H^+ + 5\,Fe^{2+} + MnO_4{}^- &\longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O \end{aligned}$$

The electric charge for the reactants $(+8 + 5 \times 2 - 1 = +17)$ is equal to the electric charge for the products $(+2 + 5 \times 3 = +17)$. This is a very quick way to check the balanced equations.

EXERCISE 15-8

Write balanced equations for these reactions by finding the half-reaction equations in Appendix 4.

(a) $Cr_2O_7{}^{2-} + Hg \longrightarrow Cr^{3+} + Hg^{2+}$

(b) $MnO_4{}^- + H_2O_2 \longrightarrow Mn^{2+} + O_2$

(c) $H_2O_2 + SO_2 \longrightarrow 2\,H^+ + SO_4{}^{2-}$

Method III Devise Half-Reactions

Many examples of redox reactions are too complicated to balance by the inspection method. Yet if the needed half-reaction equations are not in the table in Appendix 4, then another method is needed to balance the equation. Consider the reaction between zinc metal and sodium vanadate. As usual, write the reactants and products.

$$Zn + VO_3^- \longrightarrow VO^{2+} + Zn^{2+}$$

The equation for the zinc half-reaction can be written easily either by inspection or by looking in Appendix 4.

$$Zn \longrightarrow Zn^{2+} + 2\,e^-$$

The equation for the vanadate half-reaction does not appear in Appendix 4. Here is a simple procedure to find the equation for a half-reaction.

Step 1 Begin writing the half-reaction equation by showing reactant going to product. Balance the number of V atoms (in this example, one vanadium atom appears in reactant and product).

$$VO_3^- \longrightarrow VO^{2+}$$

Step 2 *Oxygen balance.* Add H_2O to balance the number of oxygen atoms.

$$VO_3^- \longrightarrow VO^{2+} + 2\,H_2O$$

Step 3 *Hydrogen balance.* Add H^+ to balance the number of hydrogen atoms.

$$4\,H^+ + VO_3^- \longrightarrow VO^{2+} + 2\,H_2O$$

Step 4 *Charge balance.* Add e^- to balance the charge. In Step 3, the charge for the reactants equals $+4 - 1 = +3$ and for the products $+2$. We must add one electron to the reactants to achieve charge balance.

$$e^- + 4\,H^+ + VO_3^- \longrightarrow VO^{2+} + 2\,H_2O$$

This is the required half-reaction equation. Combine it with the equation for the Zn–Zn^{2+} half-reaction. Remember that the number of electrons must be the same in each equation.

$$\begin{array}{r} Zn \longrightarrow Zn^{2+} + 2\,e^- \\ 2\,e^- + 8\,H^+ + 2\,VO_3^- \longrightarrow 2\,VO^{2+} + 4\,H_2O \\ \hline 8\,H^+ + Zn + 2\,VO_3^- \longrightarrow 2\,VO^{2+} + Zn^{2+} + 4\,H_2O \end{array}$$

Final check on charge balance.

$$(+8 - 2) = +6 = (+4 + 2)$$

Here is a much more complicated example in which both half-reaction equations must be generated. The same series of steps will lead to the balanced half-reaction equations.

$$P_4 + IO_3^- \longrightarrow H_2PO_4^- + I^-$$

Step 1 Begin writing the half-reaction equations by showing reactants going to product, balancing the P and I atoms.

$$\begin{aligned} P_4 &\longrightarrow 4\ H_2PO_4^- \\ IO_3^- &\longrightarrow I^- \end{aligned}$$

Step 2 *Oxygen balance.* Add H_2O as needed to balance the number of O atoms.

$$\begin{aligned} 16\ H_2O + P_4 &\longrightarrow 4\ H_2PO_4^- \\ IO_3^- &\longrightarrow I^- + 3\ H_2O \end{aligned}$$

Step 3 *Hydrogen balance.* Add H^+ as needed to balance the number of H atoms.

$$\begin{aligned} 16\ H_2O + P_4 &\longrightarrow 4\ H_2PO_4^- + 24\ H^+ \\ 6\ H^+ + IO_3^- &\longrightarrow I^- + 3\ H_2O \end{aligned}$$

Step 4 *Charge balance.* Add e^- as needed to balance the charge.

$$\begin{aligned} 16\ H_2O + P_4 &\longrightarrow 4\ H_2PO_4^- + 24\ H^+ + 20\ e^- \\ 6\ e^- + 6\ H^+ + IO_3^- &\longrightarrow I^- + 3\ H_2O \end{aligned}$$

These are the required half-reaction equations. Combine them after making the number of electrons the same in each equation. In this example, we need 60 e^- in each equation.

$$\begin{array}{rcl} 48\ H_2O + 3\ P_4 & \longrightarrow & 12\ H_2PO_4^- + 72\ H^+ + 60\ e^- \\ 60\ e^- + 60\ H^+ + 10\ IO_3^- & \longrightarrow & 10\ I^- + 30\ H_2O \\ \hline 18\ H_2O + 3\ P_4 + 10\ IO_3^- & \longrightarrow & 10\ I^- + 12\ H_2PO_4^- + 12\ H^+ \end{array}$$

Final check on charge balance

$$\begin{aligned} 0 + 0 - 10 &= -10 - 12 + 12 \\ -10 &= -10 \end{aligned}$$

EXERCISE 15-9

Write balanced equations for these redox reactions using Method III.

(a) $N_2H_5^+ + PuO_2^{2+} \longrightarrow Pu^{4+} + N_2$
(b) $Zn + NO_3^- \longrightarrow NH_4^+ + Zn^{2+}$
(c) $S_2O_6^{2-} + BiO_3^- \longrightarrow Bi^{3+} + SO_4^{2-}$

15-12 Oxidation Numbers

When metallic iron is oxidized, two electrons are given up as ferrous ion, Fe^{2+}, forms. Then when ferrous ion is oxidized, another electron must be given up as ferric ion, Fe^{3+}, forms. Chemists have found it useful to assign *oxidation numbers* to atoms or ions that enter into redox reactions.

Fe oxidation number = 0
Fe^{2+} oxidation number = +2
Fe^{3+} oxidation number = +3

Iron as the element is electrically neutral. The oxidation number assignment of zero is easy to understand. Since negative charge is carried away by the electrons, assignment of positive oxidation numbers are given to ferrous and ferric ions.

When chlorine is reduced to chloride ion, each atom in the molecule gains one electron. The oxidation numbers for chlorine and chloride are zero and −1. Often, the oxidation number for an element is not quite as obvious as in these examples. Manganese and some of its compounds can serve to illustrate the problem. What would the oxidation number be for Mn in each of these substances?

Mn oxidation number = 0
Mn^{2+} oxidation number = +2
MnO_2 oxidation number = ?
$KMnO_4$ oxidation number = ?

There is no difficulty in assigning oxidation numbers for manganese as the element, Mn, or as the ion, Mn^{2+}. How do we assign oxidation numbers to manganese and oxygen in MnO_2? Since MnO_2 is a neutral compound, the oxidation numbers for the three atoms must add up to zero. If an oxidation number is assigned to oxygen in MnO_2, the oxidation number for manganese can be calculated quite readily.

If oxidation number of oxygen is	oxidation number of manganese is
0	0
−1	+2
−2	+4
−3	+6

The first two values for manganese in MnO_2 do not seem reasonable. Manganese dioxide, MnO_2, does not have the chemical properties exhibited by metallic manganese or by Mn^{2+} ion. How can we decide whether +4 or +6 (or some other value) is a reasonable oxidation number for manganese in MnO_2? Chemists have agreed on a set of rules to follow in assigning oxidation numbers.

(1) The *oxidation number* for atoms in their elementary state is zero.

(2) The oxidation number for any monatomic species is the net charge on the atom or ion.

(3) The oxidation number for oxygen is -2 in all its compounds (except in peroxides where it is -1).

(4) The oxidation number for hydrogen is $+1$ in all its compounds (except in hydrides where it is -1).

(5) All other oxidation numbers are assigned so that the sum of oxidation numbers equals the net charge on the molecule or ion.

A few examples will illustrate the use of these rules. What will be the oxidation number for manganese in potassium permanganate, $KMnO_4$? This salt ionizes to form K^+ and MnO_4^- ions. Apply Rule 5 to find the oxidation number (Ox. No.) of manganese in MnO_4^-.

$$\text{Ox. No. Mn} + 4(\text{Ox. No. O}) = -1$$

Rule 3 helps us:

$$\begin{aligned} \text{Ox. No. Mn} + 4(-2) &= -1 \\ \text{Ox. No. Mn} &= +7 \end{aligned}$$

The dichromate ion has the formula $Cr_2O_7^{2-}$. What is the oxidation number for Cr in this ion? The sum of the oxidation numbers for the two Cr and seven O atoms must = -2, the charge on the dichromate ion.

$$\begin{aligned} 2(\text{Ox. No. Cr}) + 7(\text{Ox. No. O}) &= -2 \\ 2(\text{Ox. No. Cr}) + 7(-2) &= -2 \\ 2(\text{Ox. No. Cr}) &= +12 \\ \text{Ox. No. Cr} &= +6 \end{aligned}$$

EXERCISE 15-10

Nitrogen forms a large number of compounds with hydrogen and oxygen. Calculate the oxidation numbers for N in these compounds.

NH_3, N_2O, NO_2, N_2O_4, NO_2^-, HNO_3

EXERCISE 15-11

Calculate the oxidation numbers for P in these acids.

H_3PO_2, H_3PO_3, H_3PO_4

Chemists sometimes use oxidation numbers in naming compounds. For example, iron forms two different compounds with chlorine. It is important to distinguish one from the other, both with chemical symbols and with words. In this book, the three systems indicated in this example are used at various times.

$FeCl_2$	$FeCl_3$
Ferrous chloride	Ferric chloride
Iron dichloride	Iron trichloride
Iron(II) chloride	Iron(III) chloride

The endings -ous and -ic survive from the early days of chemistry when fewer compounds were known. This system is suitable when only two compounds are known for the pair of elements. In such cases, the endings -ous and -ic are used to modify the element name and indicate lower and higher oxidation number. Cuprous chloride is $CuCl$; cupric chloride is $CuCl_2$.

The prefixes di- and tri- distinguish between the two iron chlorides. Some other examples using prefixes to name compounds are shown below.

NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
N_2O_4	Dinitrogen tetraoxide
N_2O_5	Dinitrogen pentaoxide

The third approach to naming compounds is called the Stock system, after the chemist who first suggested this method. Roman numerals are used to tell the oxidation number for the principal element or ion. Chemists use all three ways to name a compound and we have done the same thing in this book. For rather complex substances, the Stock system provides an unambiguous name. Here are two examples.

$Fe(SCN)(H_2O)_5^{2+}$	pentaaquothiocyanoiron(III) ion
$CrCl_2(NH_3)_4^{+}$	dichlorotetraaminochromium(III) ion

15-13 Review

An understanding of what chemists mean by the words oxidation and reduction has been developed in this chapter. The operation of an electrochemical cell brings out the essential features of oxidation-reduction reactions.

Oxidation takes place at the anode of an electrochemical cell as electrons are released to the external circuit. Oxidation corresponds to the *loss of electrons.*

Reduction takes place at the cathode of an electrochemical cell as electrons are accepted from the external circuit. Reduction corresponds to the *gain of electrons.*

Oxidation and reduction must always take place together. Electrons lost when oxidation occurs are gained when reduction occurs. Recognition that redox reactions can be interpreted as the sum of two half-reactions provides a systematic method for comparing the strength of oxidizing and reducing agents. In the discussion of Bronsted acids and bases in Chapter 14, a quantitative measure of acid strength was obtained by determining the tendency for an acid to donate a proton to the reference base H_2O. The strength of a reducing agent can be measured by determining the tendency for a reducing agent to donate an electron to the reference oxidizing agent H^+.

The quantitative scale that ranks reducing agents is expressed in terms of volts. The voltage of any electrochemical cell is a measure of the potential energy of the redox system. *A positive value for the voltage* is interpreted to mean that, at equilibrium, the concentration of the products will be greater than the concentration of reactants. *A negative value for the voltage* is interpreted to mean that, at equilibrium, the concentration of reactants will exceed the concentration of products.

Spontaneous electrochemical systems are important sources of energy. The lead storage battery and the cells used in flashlights are two examples. Nonspontaneous electrochemical systems are important for the preparation of a number of essential chemical substances: chlorine, sodium hydroxide, magnesium, aluminum, and bromine are a few examples. The word *electrolysis* is used when energy forces an electrochemical reaction in the nonspontaneous direction.

Methods to balance oxidation-reduction equations include inspection, use of the table of half-reactions, and devising the needed half-reactions. Chemical nomenclature is reviewed briefly.

Questions and Problems for Chapter 15

1

(a) If a neutral atom becomes positively charged, has it been oxidized or reduced? Write a general equation using M for the neutral atom.

(b) If an ion X^- acquires a 2− charge, has it been oxidized or reduced? Write a general equation.

2

If you wish to replate a silver spoon, would you make it the anode or cathode in a cell? Use half-reactions in your explanation. How many moles of electrons are needed to plate out 1.0 gram of Ag?

3

Figure 15-2 shows electrons leaving the Cu(s) electrode and going to the Ag(s) electrode. Experimentally, both half-cells are found to be electrically neutral before current flows and to remain so as the cell operates. Explain this.

4

Equations for two half-reactions taking place in an electrochemical cell are:

$$Fe \longrightarrow Fe^{2+} + 2\,e^- \qquad 2\,e^- + Sn^{2+} \longrightarrow Sn$$

Which metal serves as the anode? Which the cathode?

5

Equations for two half-reactions taking place in an electrochemical cell are:

$$Cr \longrightarrow Cr^{3+} + 3\,e^-$$
$$2\,e^- + Pb^{2+} \longrightarrow Pb$$

This cell is similar to the one discussed in Section 15-1, page 278. How many grams of Pb will deposit on the cathode when 1.56 grams of Cr dissolves from the anode?

6

One method of obtaining copper metal is to let a solution containing Cu^{2+} ions trickle over scrap iron. Write the equations for the two half-reactions. Assume Fe^{2+} forms. Indicate in which half-reaction oxidation is taking place.

7

Aluminum metal reacts with acidic solutions to liberate hydrogen gas. Write equations for the two half-reactions and the net ionic reaction.

8

When copper is placed in concentrated nitric acid, vigorous bubbling takes place as a brown gas is evolved. The copper disappears and the solution changes from colorless to a greenish-blue. The brown gas is nitrogen dioxide, NO_2, and the solution's color is due to the formation of cupric ion, Cu^{2+}. Using half-reactions from Appendix 4, write the net equation for this reaction.

9

In acid solution the following are true: H_2S will react with oxygen to give H_2O and sulfur. H_2S will not react in the corresponding reaction with selenium or tellurium. H_2Se will react with sulfur giving H_2S and selenium but it will not react with tellurium. Arrange the hydrides of column VI, H_2O, H_2S, H_2Se, and H_2Te, in order of their tendency to lose electrons to form the elements, O_2, S_8, Se_8, and Te_8.

10

How many coulombs are needed to form 1 mole of Ag from a 1 *M* $AgNO_3$ solution?

$$Ag^+ + e^- \longrightarrow Ag$$

11

A 100 watt light bulb, when operated in a 110 volt household circuit, has a current of 0.9 amperes flowing through it. In one minute, how many electrons pass through the light bulb?

12

A flashlight bulb will burn out almost instantly if connected to a 110 volt household circuit. This does not happen if a 1½ volt dry cell is connected to the bulb. Explain.

13

If a copper wire carries a 0.1 ampere current, how many moles of electrons pass through the wire each second?

14

Complete the following equations. Determine the net voltage of each cell and decide whether reaction can occur.

(a) $Zn + Ag^+ \longrightarrow$
(b) $Cu + Ag^+ \longrightarrow$
(c) $Sn + Fe^{2+} \longrightarrow$
(d) $Hg + H^+ \longrightarrow$

15

For each of the following,

(i) write the equations for the half-reactions;
(ii) determine the net equation;
(iii) predict whether the reaction can occur, giving the basis for your prediction:

(a) $Mg(s) + Sn^{2+} \longrightarrow$
(b) $Mn(s) + Cs^+ \longrightarrow$
(c) $Cu(s) + Cl_2(g) \longrightarrow$
(d) $Zn(s) + Fe^{2+} \longrightarrow$
(e) $Fe(s) + Fe^{3+} \longrightarrow$

16

A half-cell consisting of a palladium rod dipping into a 1 *M* $Pd(NO_3)_2$ solution is connected with a standard hydrogen half-cell. The cell voltage is 0.99 volt and the platinum electrode in the hydrogen half-cell is the anode. Determine $E°$ for the reaction

$$Pd \longrightarrow Pd^{2+} + 2\,e^-$$

17

Suppose chemists had chosen the reference reaction to be $2\,I^- \longrightarrow I_2 + 2\,e^-$ with zero potential.

(a) What would $E°$ have been for $Na \longrightarrow Na^+ + e^-$?

(b) How much would the net potential have been changed for the reaction

$$2\,Na + I_2 \longrightarrow 2\,Na^+ + 2\,I^-$$

18

If a piece of copper metal is dipped into a solution containing Cr^{3+} ions, what will happen? Explain, using $E°$ values.

19

What will happen if an aluminum spoon is used to stir an $Fe(NO_3)_2$ solution? What will happen if an iron spoon is used to stir an $AlCl_3$ solution?

20

Can 1 *M* $Fe_2(SO_4)_3$ solution be stored in a container made of nickel metal? Explain your answer.

21

In Section 15-6, the reaction of iron with a solution of nickel ions was discussed. Will the reaction

$$2\,Fe^{2+} + Ni^{2+} \longrightarrow 2\,Fe^{3+} + Ni$$

occur? What is the net voltage?

22

Most of the bromine produced in the United States is made by oxidizing Br^- to Br_2 using Cl_2. What is $E°$ for this reaction?

23

Which of the half-reactions will spontaneously reduce Cu^{2+} to Cu(s)?

(a) Sn^{2+} to Sn^{4+}

(b) Cl^- to $Cl_2(g)$

(c) Au to Au^{3+}

(d) MnO_4^- to Mn^{2+}

(e) Ag to Ag^+

24

Which of the half-reactions will spontaneously oxidize Fe^{2+} to Fe^{3+}?

(a) Ag^+ to Ag

(b) Pb^{2+} to Pb

(c) Al^{3+} to Al

(d) MnO_4^- to Mn^{2+}

(e) Li to Li^+

25

The four elements W, X, Y, and Z form diatomic molecules and also form singly charged negative ions. The following observations are made in a series of experiments.

$2\,X^- + Y_2$ gives $2\,Y^- + X_2$
$2\,W^- + Y_2$ no reaction
$2\,Z^- + X_2$ gives $2\,X^- + Z_2$

Use these observations to write equations for each oxidation half-reaction. Arrange them in a short oxidation potential series. Which ion is the strongest reducing agent? Which molecule is the strongest oxidizing agent?

26

In the electrolysis of aqueous cupric bromide, $CuBr_2$, 0.500 gram of copper is deposited at one electrode. How many grams of bromine are formed at the other electrode? Write the anode and cathode half-reactions.

27

Determine the oxidation number of uranium in each of these known compounds: UO_3, U_3O_8, U_2O_5, UO_2, UO, K_2UO_4, MgU_2O_7.

28

Write a balanced equation for the reaction between stannous ion, Sn^{2+}, and permanganate ion, MnO_4^-, in acid solution to produce stannic ion, Sn^{4+}, and manganous ion, Mn^{2+}.

29

Use Appendix 4 to write a balanced equation for each of the following reactions:

(a) $H_2O_2 + I^- + H^+$ gives $H_2O + I_2$
(b) $Cr_2O_7^{2-} + Fe^{2+} + H^+$ gives $Cr^{3+} + Fe^{3+} + H_2O$
(c) $Cu + NO_3^- + H^+$ gives $Cu^{2+} + NO + H_2O$

30

Give a balanced equation for each of the following reactions:

(a) $HBr + H_2SO_4$ gives $SO_2 + Br_2 + H_2O$
(b) $NO_3^- + Cl^- + H^+$ gives $NO + Cl_2 + H_2O$
(c) $Zn + NO_3^- + H^+$ gives $Zn^{2+} + NH_4^+ + H_2O$
(d) BrO^- gives $Br^- + BrO_3^-$

31

Iodine is recovered from iodates in Chile saltpeter by the reaction

$$HSO_3^- + IO_3^- \text{ gives } I_2 + SO_4^{2-} + H^+ + H_2O$$

(a) How many grams of sodium iodate, $NaIO_3$, react with 1.00 mole of $KHSO_3$?
(b) How many grams of iodine, I_2, are produced?

32

The chlorine used to purify your drinking water was probably made by electrolyzing molten NaCl to produce liquid sodium and gaseous chlorine.

(a) How many grams of sodium chloride are needed to produce 355 grams of chlorine gas?
(b) What volume would this gas occupy at STP?

33

A 6 volt lead storage battery contains 700 grams of pure $H_2SO_4(l)$ dissolved in water.

(a) How many grams of solid sodium carbonate, Na_2CO_3, would be needed to neutralize this acid (giving CO_2 gas and H_2O) if it were spilled?
(b) How many liters of 2.0 *M* Na_2CO_3 solution would be needed?

34

Nitric acid, HNO_3, is made by the process

$$3\,NO_2(g) + H_2O(l) \rightleftharpoons 2\,HNO_3(l) + NO(g)$$

Commercial concentrated acid contains 68% by weight HNO_3 in water. The solution is 15 *M*. How many liters of concentrated acid are needed to react with 0.100 kg of copper metal?

$$Cu + H^+ + NO_3^- \text{ gives } Cu^{2+} + NO_2 + H_2O$$

Answer: 0.42 liter of HNO_3

35

How many grams of silver metal will react with 2.0 liters of 6.0 *M* HNO_3? The reactants and products are

$$Ag + H^+ + NO_3^- \text{ gives } Ag^+ + NO + H_2O$$

36

How many milliliters of a 0.050 *M* $KMnO_4$ solution are required to oxidize 2.00 grams of $FeSO_4$ in a dilute acid solution?

Answer: 53 ml of $KMnO_4$ solution

Molecular Structure

16

There are always three questions a chemist hopes to answer when he has synthesized a new compound.

> Which elements, in what amounts, are present in this compound?
>
> How many atoms of each element occur in one molecule?
>
> How are the atoms arranged in the molecule?

During the nineteenth century, methods of chemical analysis were developed that led to answers for the first question. In order to answer the second question the molar mass of the new substance must be determined. Avogadro's Hypothesis provided the first method to find the molar mass for a gas. The mass of a particular volume of a gas is compared with the mass of the same volume of a reference gas, such as oxygen, at the same temperature and pressure. You made such a measurement in Experiment 5.

Finding out how the atoms in a molecule are arranged is the most difficult and also the most important problem in identifying an unknown compound. The search for an answer to this question can be as exciting as a detective story, with the chemical and physical properties of the compound furnishing the clues. With the right collection of clues, the chemist can establish the molecular structure of the substance he has synthesized. This phase of chemistry has developed slowly and carefully over the last one hundred years. First, the structure of simple molecules had to be established. One great step in arriving at an understanding of molecular structure was the proposal made in 1858 by a German chemist, August Kekulé. He knew that carbon atoms form compounds such as methane and carbon tetrachloride, CH_4 and CCl_4. Kekulé generalized when he suggested that carbon atoms form four bonds in all carbon compounds. He also proposed that many carbon compounds contained rings of carbon atoms. These two ideas helped chemists determine the structures of many molecules. Since Kekulé's time, a large number of structures have been established. Today the immense store of known molecular structures helps chemists to determine the structures of very complex molecules, many of great importance in biological systems.

The chemical methods that have been used to establish molecular structure will be presented in the first half of this chapter. The majority of structural information that has been collected for molecules came from these methods. In the second half of the chapter several important physical methods of determining structure are discussed. These methods provide quantitative information about bond angles, bond distances, and bond energies. Do not forget, however, that these approaches to molecular structure became possible only after the structures of many simple molecules were known and used as standards against which the physical method could be tested.

CHEMICAL METHODS OF STRUCTURE DETERMINATION

16-1 Different Kinds of Formulas

Let us repeat the three questions posed above.

> Which elements, in what amounts, are present in this compound?
>
> How many atoms of each element occur in one molecule?
>
> How are the atoms arranged in the molecule?

The steps a chemist follows to find answers to these questions are illustrated with ethane and ethanol, two carbon compounds.

Ethane is a gas that is often contained in the household gas used for heating and cooking. Its chemistry is almost wholly restricted to the combustion reaction. Ethanol is a liquid that takes part in a variety of useful chemical reactions. It has great value in the manufacture of chemicals, and it bears little chemical resemblance to ethane. Yet, the similarity of the two names, *ethane* and *ethanol,* suggests that these compounds are related. This is true. Their molecular structures will help us understand how they are related and, at the same time, why their properties are so different. We must find out *what kinds of atoms* are present in each substance, *how many atoms* there are per molecule, and their *bonding arrangement.* Usually many experiments need to be performed before the molecular structure of a compound is known with certainty. This fascinating problem involves three basic experimental steps: to determine the *empirical formula,* then the *molecular formula,* and finally, the *structural formula.* First the information conveyed by each of these formulas will be reviewed, with ethane as the example. Then we will consider the experiments used in the determination of each type of formula, with ethanol as the example.

The **empirical formula** tells the *relative number* of atoms of each element in a molecule. Analysis of ethane shows that this is a compound of carbon and hydrogen. For each 3 g of hydrogen, there are 12 g of carbon.

$$\text{Number of moles of H atoms} = \frac{3\text{ g}}{1\text{ g/mole H atoms}} = 3\text{ moles}$$

$$\text{Number of moles of C atoms} = \frac{12\text{ g}}{12\text{ g/mole C atoms}} = 1\text{ mole}$$

Therefore the empirical formula for ethane is CH_3.

The **molecular formula** shows the *total number* of each kind of atom in the molecule. Measurements similar to those you carried out in Experiment 5 indicate that the molar mass of ethane is 30 grams. This molar mass together with the empirical formula tells us the molecular formula. The molecular formula must be some multiple of the empirical formula.

$(CH_3)_1$	corresponds to a molar mass of 15 grams
$(CH_3)_2$	corresponds to a molar mass of 30 grams
$(CH_3)_3$	corresponds to a molar mass of 45 grams

Ethane has the molecular formula of $(CH_3)_2$, usually written C_2H_6.

EXERCISE 16-1

Write the molecular formula for the carbon-hydrogen compound having the empirical formula CH_2 and a molar mass of 28 grams.

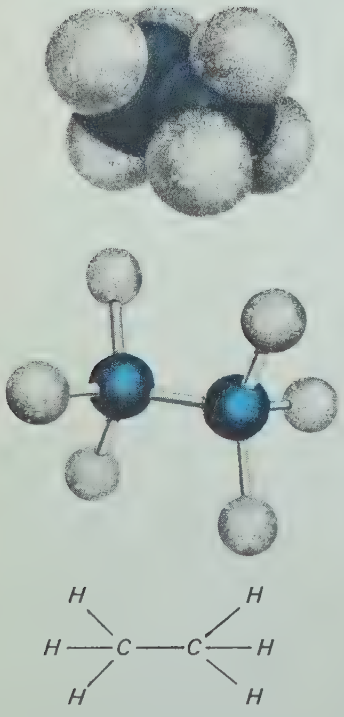
The proposals Kekulé made can be used to obtain the **structural formula** from the molecular formula, C_2H_6.

> A carbon atom forms four bonds and may bond to another carbon atom.
>
> A hydrogen atom forms only one bond.

How can these 8 atoms be arranged in the molecule C_2H_6? There is only one way to do this using the above rules. Several different representations of the structural formula for ethane are shown in Figure 16-1. The choice of which formula to use depends upon the structural feature to be emphasized. The first and second drawings emphasize the three-dimensional nature of ethane. The third is a simpler way of doing the same thing. The last formula merely shows that three hydrogens are attached to each carbon atom.

16-2 The Determination of the Structure of Ethanol

Three steps are necessary in arriving at the molecular structure of a compound. What experiments are important in each of these steps?



CH_3CH_3

FIGURE 16-1

Various representations of ethane, C_2H_6.

Step 1. Which elements, in what amounts, are present in ethanol?

A known mass of this compound is burned in oxygen. The products are CO_2 and H_2O, showing that carbon and hydrogen were present in ethanol. The mass of the carbon dioxide reveals how much carbon was in the sample. The mass of water reveals how much hydrogen was in the sample. The remainder of the sample is taken to be oxygen as no other elements occur in the products.

Suppose 46 grams of ethanol are burned. Collection of the products yields 88 grams of carbon dioxide and 54 grams of water. We want to know the relative numbers of carbon, hydrogen, and oxygen atoms in the compound. This can be obtained by calculating the number of moles of carbon dioxide and water produced by the combustion of the 46-gram sample.

$$\text{Number of moles } CO_2 = \frac{88\text{ g}}{\text{molar mass } CO_2} = \frac{88\text{ g}}{44\text{ g/mole}} = 2.0\text{ moles}$$

$$\text{Number of moles } H_2O = \frac{54\text{ g}}{\text{molar mass } H_2O} = \frac{54\text{ g}}{18\text{ g/mole}} = 3.0\text{ moles}$$

Now the following statements can be made about ethanol:

Burning 46 grams of ethanol yields two moles of CO_2 and three moles of H_2O

or

46 grams of ethanol contain two moles of carbon atoms and six moles of hydrogen atoms

or

46 grams of ethanol contain 24 grams of carbon atoms and 6 grams of hydrogen atoms.

Thirty grams of the original 46 grams are accounted for. The remainder of the sample (46 − 30 or 16 grams) must have been oxygen. This corresponds to

$$\frac{16\text{ g}}{\text{molar mass of oxygen atoms}} = \frac{16\text{ g}}{16\text{ g/mole}} = 1.0\text{ mole of oxygen atoms}$$

Summarizing, 46 grams of the compound ethanol contain

two moles of carbon atoms,
six moles of hydrogen atoms,
one mole of oxygen atoms.

These results give the empirical formula, C_2H_6O.

EXERCISE 16-2

Automobile antifreeze often contains a compound called ethylene glycol. Analysis of pure ethylene glycol shows that it contains only

(*Exercise 16-2 continued on p. 316.*)

(Exercise 16-2 continued from p. 315.)

carbon, hydrogen, and oxygen. A sample of ethylene glycol was burned and the following results were obtained.

mass of sample burned = 15.5 mg
mass of CO_2 formed = 22.0 mg
mass of H_2O formed = 13.5 mg

What is the empirical formula of ethylene glycol?

Step 2. How many atoms of each element occur in one molecule of ethanol?

We know that the relative numbers of atoms in ethanol are two carbon to six hydrogen to one oxygen. But is the molecular formula C_2H_6O or $C_4H_{12}O_2$ or $C_6H_{18}O_3$ or some other multiple of the empirical formula, C_2H_6O?

An experiment to measure the molar mass will help in answering this question. Ethanol is a liquid at room temperature but ethanol vapor is needed to determine the molar mass by the method used in Experiment 5. A weighed amount of liquid is placed in a gas collecting device held at an easily regulated temperature. For example, a steam condenser around the device provides a convenient way of holding the temperature at 100°C. When the substance has vaporized completely, its pressure and volume are measured. This measurement gives the mass per unit volume of gaseous ethanol at a known temperature and pressure. The mass is then compared with the mass of the same volume of a reference gas (usually O_2) at the same temperature and pressure.

Such a measurement shows that a given volume of ethanol at 100°C and one atmosphere weighs about 1.5 times as much as the same volume of oxygen gas at the same conditions. Avogadro's Hypothesis states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. Therefore, the molar mass for ethanol is 1.5 times the molar mass of oxygen.

$$\begin{aligned}\text{Molar mass (ethanol)} &= 1.5 \times \text{molar mass } O_2\\ &= 1.5 \times 32\\ &= 48 \text{ grams}\end{aligned}$$

Even though this number may not have been measured with high precision, it shows clearly what multiple of the empirical formula to choose.

Molecular Formula	Molar Mass	Experimental Value for Molar Mass
C_2H_6O	46.07 grams	48 grams
$C_4H_{12}O_2$	92.14 grams	
$C_6H_{18}O_3$	138.21 grams	

For ethanol the molecular formula is C_2H_6O, the same as the empirical formula.

EXERCISE 16-3

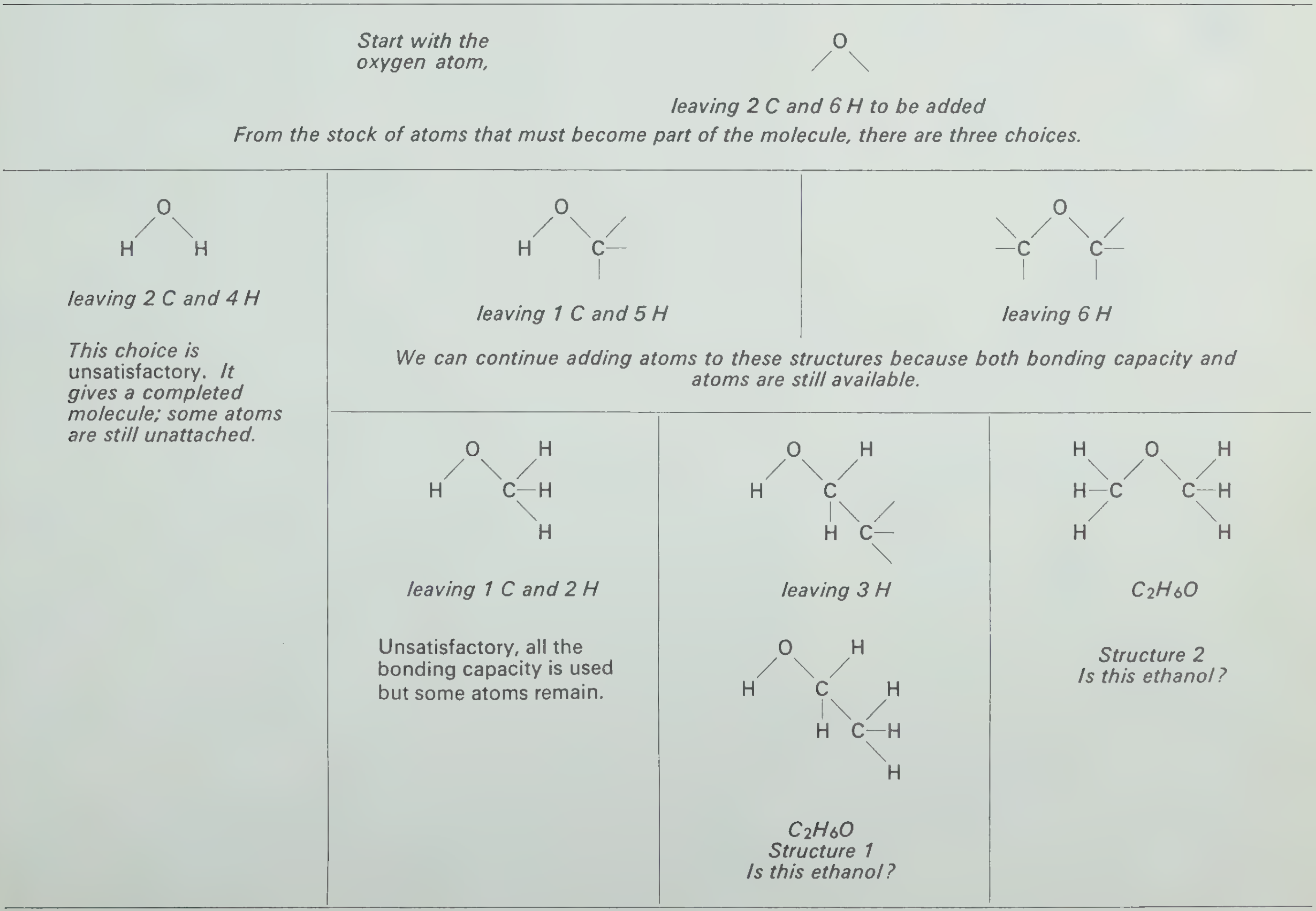
Ethylene glycol, the example treated in Exercise 16-2, has an empirical formula of CH_3O. A sample weighing 0.49 gram is vaporized completely at 200°C and at one atmosphere pressure. The volume measured under these conditions is 291 ml. The same volume of oxygen gas at the same conditions weighs 0.240 gram. Is the molecular formula for ethylene glycol CH_3O or $C_2H_6O_2$ or $C_3H_9O_3$ or some higher multiple of CH_3O?

Step 3. How are the atoms arranged in ethanol?

The determination of the bonding arrangement in a molecule is the most important problem in identifying an unknown compound. How can we proceed? Each molecule of ethanol contains two carbon, one oxygen, and six hydrogen atoms. In proposing a

FIGURE 16-2

Development of possible structures for a compound with the molecular formula C_2H_6O



Start with the oxygen atom,

leaving 2 C and 6 H to be added

From the stock of atoms that must become part of the molecule, there are three choices.

leaving 2 C and 4 H

This choice is unsatisfactory. It gives a completed molecule; some atoms are still unattached.

leaving 1 C and 5 H

leaving 6 H

We can continue adding atoms to these structures because both bonding capacity and atoms are still available.

leaving 1 C and 2 H

Unsatisfactory, all the bonding capacity is used but some atoms remain.

leaving 3 H

C_2H_6O
Structure 1
Is this ethanol?

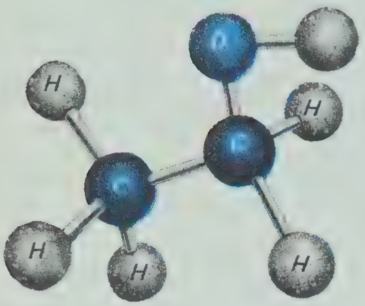
C_2H_6O

Structure 2
Is this ethanol?

molecular structure, a good guide is that carbon will form four bonds, oxygen two bonds, and hydrogen one bond. Finally, the proposed formula must fit the chemical behavior of ethanol.

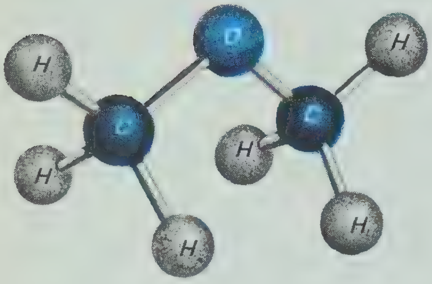
We can start with the oxygen atom and see how a molecule might be built around it. There are two carbon atoms and six hydrogen atoms at our disposal. In Figure 16-2, the gradual construction of the possible structure is shown. The atoms remaining to be connected are listed below each stage of the construction. Two possible structures result and are shown in Figure 16-3. Compounds with the same molecular formula but different structural formulas are called **isomers.** The existence of both compounds 1 and 2 was known long before their structures were clarified. Hence the existence of these isomers perplexed chemists for decades.

Structure 1



CH_3CH_2OH

Structure 2



CH_3OCH_3

FIGURE 16-3
Structure of the isomers of C_2H_6O.

EXERCISE 16-4

Ethylene glycol has the empirical formula CH_3O and the molecular formula $C_2H_6O_2$. Using the usual bonding rules draw some of the possible structural formulas for this compound.

The problem now is to decide whether ethanol has structure 1 or structure 2. How can we tell which is correct? What preliminary ideas can be obtained from an examination of the structural formulas?

In structure 2, all of the hydrogen atoms are the same. Each hydrogen atom is bonded to a carbon atom which is, in turn, bonded to the oxygen atom. In structure 1, one of the hydrogen atoms is quite different from any of the others: it is bonded to oxygen and not to carbon. Of the remaining five hydrogen atoms, two are placed on the carbon which is bonded to oxygen, and three are on the other carbon. Structures 1 and 2 should have quite different properties. Which structure agrees with the chemistry of ethanol?

There are several kinds of evidence. Some comes from the behavior of ethanol in chemical reactions and some from the determination of certain physical properties. Consider the chemical reactions first.

Sodium metal reacts vigorously with ethanol, giving hydrogen gas. An ionic compound, sodium ethoxide, with empirical formula C_2H_5ONa also forms in the reaction. Sodium metal also reacts vigorously with water to produce hydrogen gas and an ionic compound, sodium hydroxide, NaOH. This similarity in reaction suggests that ethanol has some structural relation to water. In water there are two hydrogen atoms bonded to one oxygen atom. In structure 1 there is one hydrogen atom bonded to oxygen. This chemical evidence suggests ethanol has structure 1.

Quantitative evidence can be obtained by carrying out the reaction between an excess of sodium and a weighed amount of ethanol, measuring the amount of hydrogen gas evolved. It is found that one mole of ethanol produces one half mole of hydrogen gas. A balanced chemical equation can be written for the reaction of sodium with ethanol.

$$Na + C_2H_6O \longrightarrow \tfrac{1}{2} H_2 + C_2H_5ONa$$

Apparently one molecule of ethanol contains one hydrogen atom that is capable of reacting with sodium and five that are not. Consider structures 1 and 2 in the light of this information. In structure 2 all six of the hydrogen atoms are structurally equivalent. In structure 1 there is one hydrogen atom in the molecule different from the other five. One hydrogen is bonded to the oxygen atom; five hydrogen atoms are bonded to carbon atoms. Structure 1 agrees with the experimental fact that only one hydrogen atom in ethanol will react with sodium. Structure 2 does not.

There is further evidence that CH_3CH_2OH is the correct structural formula for ethanol. Compounds containing only carbon and hydrogen do not react readily with metallic sodium to produce hydrogen gas. In these compounds, called hydrocarbons, the hydrogen atoms are bonded to carbon atoms. The deduction can be made that hydrogen atoms bonded to carbon atoms do not react with sodium to produce hydrogen gas. In structure 2, CH_3OCH_3, all the hydrogen atoms are bonded to carbon atoms. We do not expect a compound with this structure to react with sodium. Ethanol reacts with sodium. Therefore, it is unlikely that ethanol has structure 2.

Consider one other reaction of ethanol. If ethanol is heated with aqueous HBr, a volatile compound is formed. This compound is only slightly soluble in water and contains bromine. From chemical analysis and determination of the molar mass, the molecular formula is found to be C_2H_5Br, ethyl bromide. With the aid of the bonding rules, it can be seen that there is only one possible structure for this compound. This result is verified by the fact that only one isomer of C_2H_5Br has ever been discovered.

How does this chemical reaction furnish a clue to the structure of ethanol? Structure 1 could give the structural formula shown in Figure 16-4 merely by breaking the carbon-oxygen bond. It is difficult to conceive of a simple way to go from structure 2 to the structure shown for ethyl bromide.

No one fact by itself gives absolute proof of the molecular structure of a substance. In our example, combined results of different experiments show that structure 1 is the correct structure for ethanol. A comparable set of experiments shows that another compound with the formula C_2H_6O has properties consistent with structure 2. This compound is called dimethyl ether.

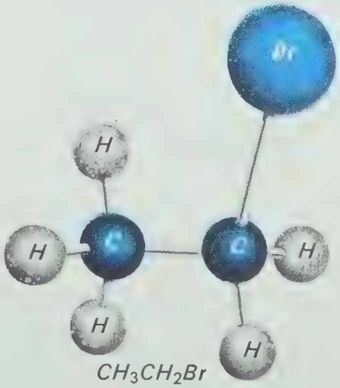


FIGURE 16-4

Structure of ethyl bromide.

EXERCISE 16-5

Find the possible structures for a compound with molecular formula C_2H_7N. Nitrogen has three unpaired electrons.

16-3 Energy and Molecular Structure

Much of the quantitative information that chemists know about molecular structure has been obtained by observing what happens when some form of energy is put into a substance. The sample may absorb the energy. It may scatter the energy. Or it may be transparent to the energy. For example, air is transparent to light in the visible part of the spectrum. Chemists try to explain these effects in terms of molecular behavior. An example from your own laboratory work will help you to understand how these interpretations are made.

Recall Experiment 12 where you studied the warming behavior of *para*dichlorobenzene. As heat energy was put into your sample, the temperature increased steadily until the melting temperature was reached. Then, even though you continued to heat the sample, the temperature remained constant for several minutes. Why do solids behave this way? Is there an explanation in terms of molecular behavior? These questions are answered by proposing that as the crystal melts a liquid forms with higher potential energy than the solid. The regular arrangement of atoms, molecules, or ions in the crystal is lost. Similar questions arise when energy in the form of light interacts with a substance. Energy can be absorbed, energy can be scattered, or energy may be transmitted through the sample undisturbed. This is represented schematically in Figure 16-5. For some energy regions, a substance may be quite transparent; that is, transmit energy. At other values of energy, the sample may exhibit strong interaction, absorbing most of the energy. Here is an analogy to help you understand what may happen.

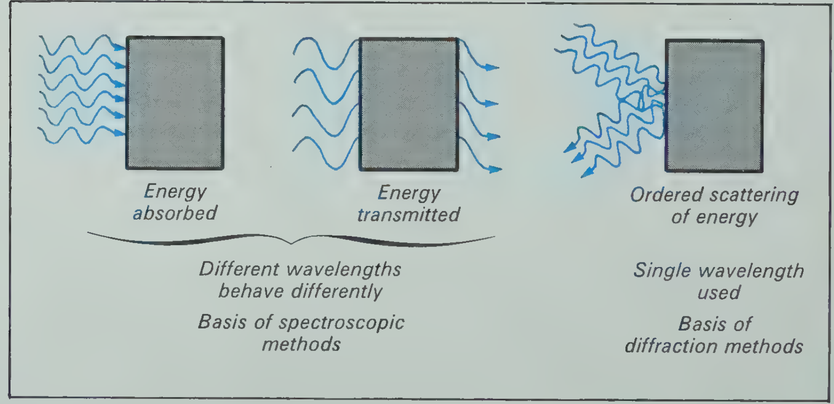

Energy absorbed
Energy transmitted
Ordered scattering of energy
Different wavelengths behave differently
Basis of spectroscopic methods
Single wavelength used
Basis of diffraction methods

FIGURE 16-5

Types of interaction between light and chemical compounds.

Suppose you are riding in a car on a smooth highway. A considerable amount of the energy produced by burning gasoline in the car engine is converted into kinetic energy of the moving car. Of course, some energy is lost in heating the car tires and wearing out the road. Some energy becomes potential energy if the car goes uphill. A close look at the surface of the road probably shows many tiny bumps and holes. However, the car and tires are so much bigger than these irregularities that very little energy is absorbed by the road. Similarly, if the highway gradually rises a mile and then gradually decreases during the next mile, the irregularity in the road, that is the hill, is much larger than the car. Once again, very little energy is lost to the road. But what happens if you are travelling on an old road which has many holes one foot in diameter? The ride becomes quite uncomfortable, perhaps even dangerous. Much of the energy that your automobile produces gets "scattered" or "absorbed" by the road. The fact that the holes or ruts get larger as cars drive over this road shows that energy is transferred from the car. Figure 16-6 illustrates the car interacting with the road.

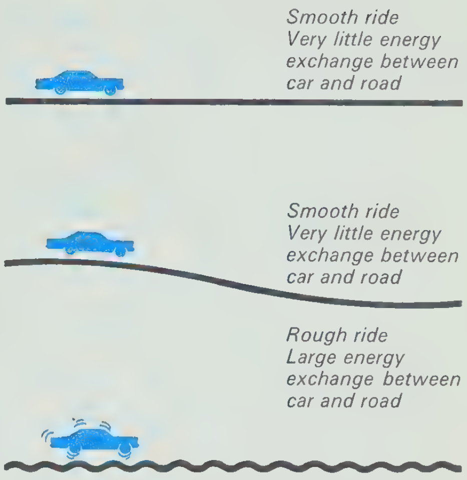

Smooth ride
Very little energy exchange between car and road
Smooth ride
Very little energy exchange between car and road
Rough ride
Large energy exchange between car and road

FIGURE 16-6

Energy exchange between a moving car and different roads.

Water and its interaction with light furnishes an example of molecular interaction with energy. Thin layers of water do not absorb appreciably in the visible region of the spectrum. You know that water in a drinking glass appears colorless. You also know that a television set operates quite normally even during a rainstorm. Apparently water does not absorb much of the energy a television station sends out. However, water interacts strongly with light in the infrared region of the spectrum. A large fraction of the infrared radiation from the sun never reaches the earth's surface because water vapor absorbs it so effectively.

A chemist tries to explain these results in terms of behavior of the molecules. In the next sections three different methods of determining molecular structure will be outlined.

16-4 Diffraction Methods

Three important methods of determining molecular structure are based on the scattering or diffraction of energy. These are X-ray diffraction, electron diffraction, and neutron diffraction. The first is most useful in studying solids while electron diffraction is applicable primarily to substances in the gas phase. Neutron diffraction is capable of locating hydrogen atoms, something that is difficult to do by either X-ray or electron diffraction. These methods complement each other. A discussion of X-ray scattering will illustrate a diffraction method.

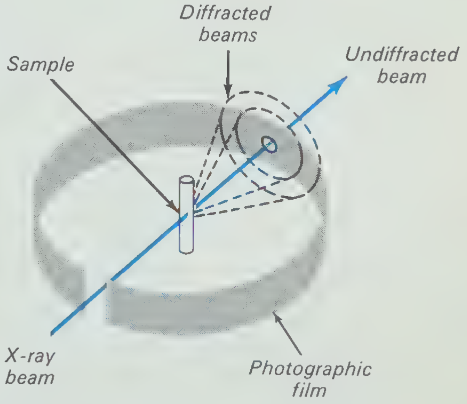


FIGURE 16-7

X-ray diffraction from a powdered sample.

X rays are very high frequency light waves, with wavelengths near 1 Ångstrom. When these waves of light fall on a crystal, diffraction through different angles occurs. The diffraction pattern can be recorded photographically. The experimental method is indicated in Figure 16-7. The observed pattern depends on the spacing of atoms or ions in the crystal and also on the wavelength of the X rays. A knowledge of the X-ray wavelength permits an interpretation of the pattern in terms of the atomic arrangement in the crystal. Figure 16-8 shows three X-ray diffraction patterns obtained from small crystals of metallic copper, aluminum, and sodium. The similarity

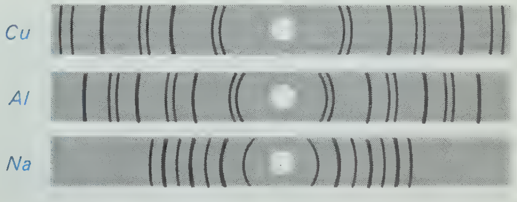


FIGURE 16-8
X-ray diffraction patterns from metallic copper, aluminum, and sodium powders.

of the patterns given by copper and aluminum shows that they have the same crystal packing. Careful measurements of the spacing of the lines indicate that the atoms in copper, though occupying the same relative positions as the atoms in aluminum, are closer together. In contrast, the pattern of lines produced by sodium does not resemble either of the preceding ones. The arrangement of sodium atoms is different from that of copper or aluminum atoms.

In the next chapter the structure of metallic and ionic solids will be discussed. The X-ray diffraction method is the principal method for finding the structure of solids.

16-5 Spectroscopic Methods

A number of important ways to determine molecular structure are based on absorption of light. These are called spectroscopic methods and differ primarily in the energy of the radiation being used. Table 16-1 presents a summary of the kind of molecular information that can be obtained by studying how molecules interact with light of different wavelengths. Infrared spectroscopy will be discussed as an example of spectroscopic measurements.

TABLE 16-1

Spectroscopic Measurements

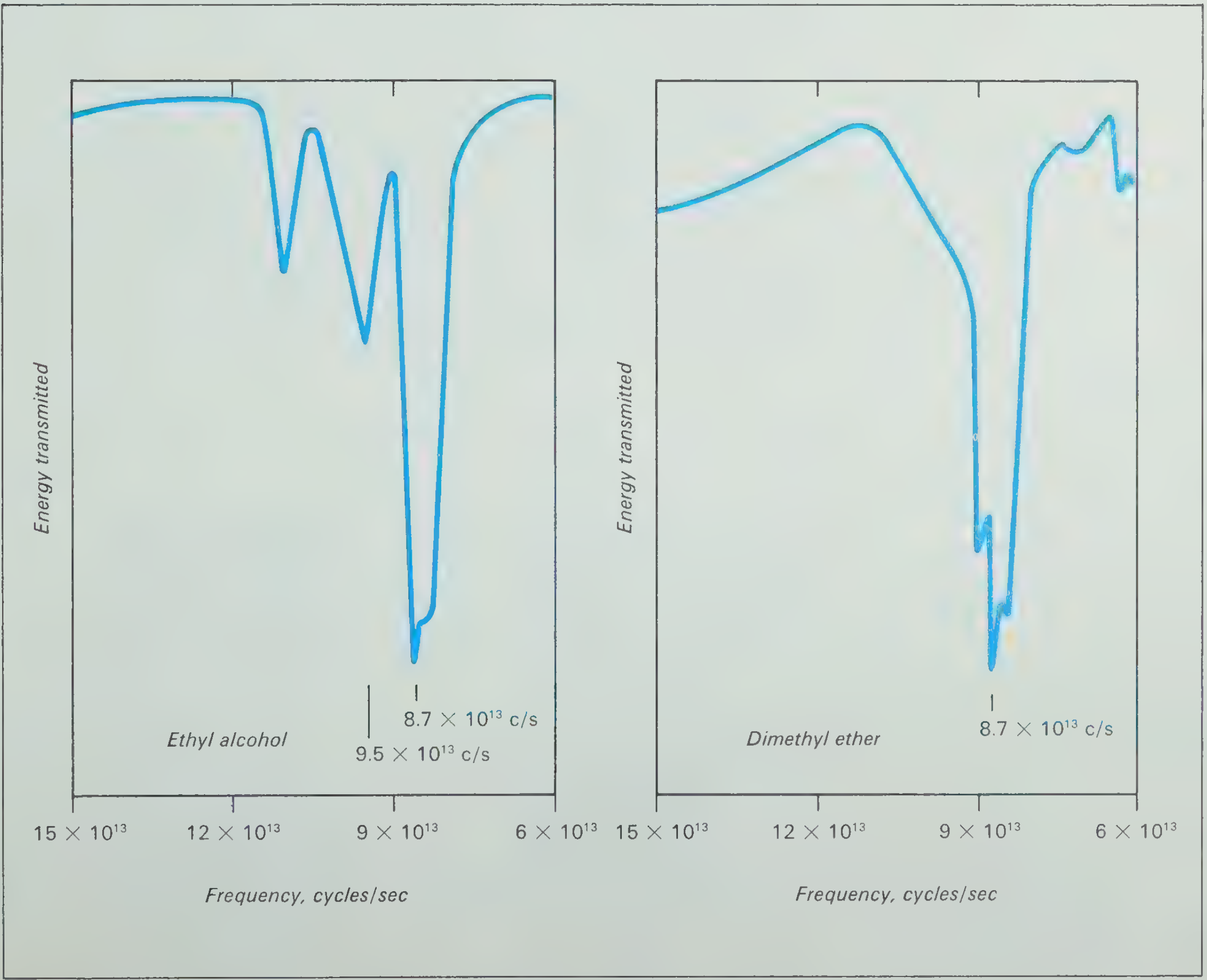
Name of Region and Wavelength	Approximate Energy, kcal/mole	Molecular Response	Derived Information
Visible and ultraviolet (10^{-4} to 10^{-5} cm)	30–300	Electronic excitation	Ionization energy Bond energy
Infrared (10^{-2} to 10^{-4} cm)	0.3–30	Atomic vibration and molecular rotation	Bond length Bond angle Bond energy
Microwave (0.1 to 10 cm)	0.0003–0.03	Molecular rotation	Bond length Bond angle

Light found in the spectrum just beyond the red end of the visible spectrum is called infrared light. Many molecules absorb light in this spectral region. Analysis of the frequencies shows that the absorptions are associated with vibrational motions of the molecules. These to-and-fro motions of the atoms occur at specific frequencies which are fixed by the masses of the atoms, the molecular shape, and the strengths of the chemical bonds that link the atoms together. The frequencies absorbed by gaseous molecules provide information about the molecular geometry and about bond energies. Because infrared studies can be extended to the liquid and solid state, it finds widespread use in chemistry.

The spectra for ethanol and dimethyl ether are presented in Figure 16-9. The horizontal scale shows frequency and the vertical scale shows the percentage of light transmitted by the sample. A reading of 100% means all of the light is transmitted. There are a number of frequencies in these spectra where only a small percent of the light passes through the sample. The frequencies where absorption of infrared light occurs are characteristic of different vibrations in a molecule. Let us look at the two frequencies 8.7×10^{13} and 9.5×10^{13} cycles per second. They correspond to the stretching vibration for the C—H and the O—H bonds, respectively. Both substances exhibit strong absorption at 8.7×10^{13} cycles per second. Both molecules have carbon-hydrogen bonds. Ethanol exhibits strong absorption at 9.5×10^{13} cycles per second but dimethyl ether is transparent to light with this frequency. This information is readily interpreted to mean that ethanol *has* an oxygen-hydrogen bond but dimethyl ether does not.

FIGURE 16-9

A portion of the infrared spectra of two C_2H_6O isomers.



You may be wondering why chemists did not use this approach to finding the molecular structure of ethanol and dimethyl ether in the first place. There are two reasons. Infrared spectrometers have become common in chemical laboratories only during the last twenty years. More important, the interpretation of complex spectra has been possible only by studying the absorption curves of simple molecules whose structures were established by chemical methods many years ago.

Infrared spectroscopy is one of the most useful methods of establishing molecular structure. In addition, infrared spectra are often very helpful in identifying substances and for checking their purity. The infrared absorption spectrum is often as important as the melting temperature for characterizing a pure substance. Usually the spectrum is more specific than the melting behavior.

16-6 Nuclear Magnetic Resonance, NMR

A relatively new method for investigating the chemical bonding in a molecule will be the last topic in this chapter. This method studies the behavior of atomic nuclei when a compound is placed in a magnetic field. Scientists call it *nuclear magnetic resonance,* or use the abbreviation NMR.

There are several reasons for the widespread use of NMR in determining molecular structure. First, the study can often be completed in a short time, an hour or a day. The X-ray diffraction method, by contrast, requires weeks or months for complete analysis of the structure of even simple molecules. Second, NMR gives information about specific bonds in a molecule. An infrared spectrum usually gives information about many bonds in a molecule and decoding the spectrum may be difficult. Let us begin the discussion of nuclear magnetic resonance by outlining briefly the basis for this method.

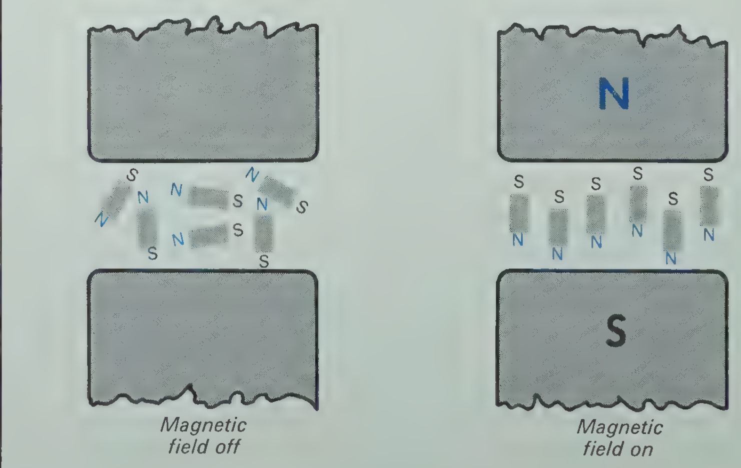
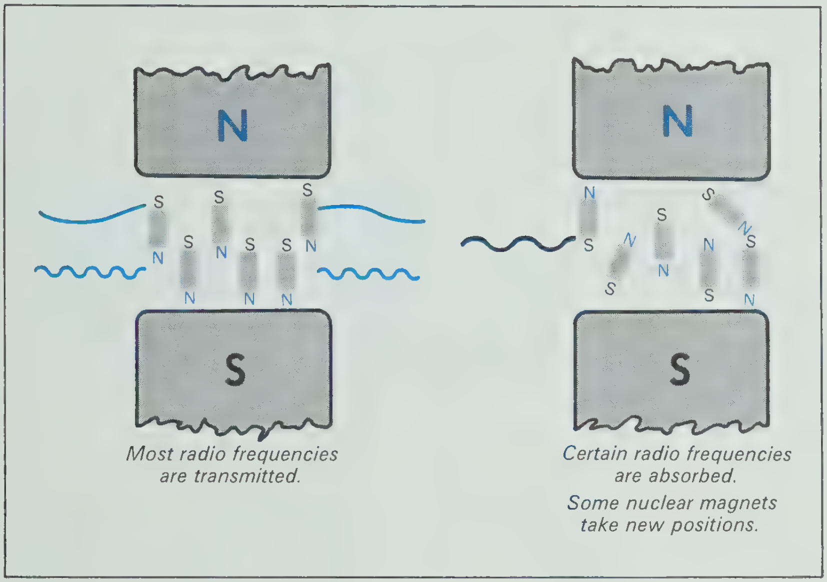


FIGURE 16-10

Schematic representation of hydrogen atom nuclear magnets in the presence and absence of a magnetic field.

The nuclei in atoms such as ${}^{1}_{1}H$ and ${}^{19}_{9}F$ behave like very small magnets with a north and a south pole. The nuclear magnets usually point in all directions as the molecules containing them move about. In the presence of a strong magnetic field these nuclear magnets reach the lowest potential energy level by lining up with the magnetic field. Figure 16-10 indicates these arrangements. Now, with the magnetic field on, energy in the form of short wavelength radio waves is passed through this sample. For radio waves that have too much or too little energy, the sample is transparent. For radio waves with just a certain energy or wavelength, the sample absorbs the energy. The energy causes some of the nuclear magnets to turn in the magnetic field. This is shown schematically in Figure 16-11.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Most radio frequencies are transmitted.
Certain radio frequencies are absorbed.
Some nuclear magnets take new positions.

FIGURE 16-11

Schematic representation of energy absorption by nuclear magnets in a magnetic field.

The importance of this method lies in the fact that the strength of the magnetic field that penetrates to the nucleus is very dependent on the electron density surrounding a particular nucleus. Because of this, the wavelength of the radio waves absorbed by a nucleus depends on the nature of the neighboring atoms and chemical bonds. The two substances, ethanol and dimethyl ether, can serve as examples.

The NMR spectrum for ethanol can be obtained by changing the wavelength of the radio waves passed through the sample. At certain wavelengths, the amount of energy absorbed increases sharply. There are three peaks A, B, and C in the NMR spectrum for ethanol shown in Figure 16-12.

The structure of ethanol is known to be CH_3CH_2OH. Note there are three different kinds of hydrogen atoms.

1 H atom attached to O
2 H atoms bound to C which is attached to C and O
3 H atoms bonded to C which is attached to C only

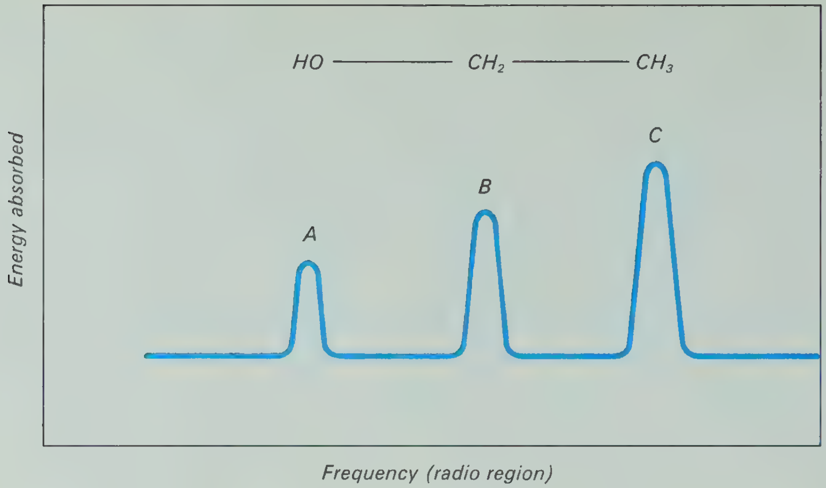


FIGURE 16-12

NMR spectrum of ethanol.

Perhaps the three peaks in the NMR spectrum result from these three kinds of hydrogen. The peak areas are in 1:2:3 ratio, the same as the numbers of the hydrogens. Similar connections between peak areas and number of hydrogens have been found for many compounds.

The NMR spectrum for dimethyl ether is compared to that of ethanol, $C_2H_5OH_3$, in Figure 16-13. The single peak can be interpreted to mean that there is a single group of protons in this substance and that all protons are in the same electron environment. The structural formula for dimethyl ether is $H_3C—O—CH_3$.

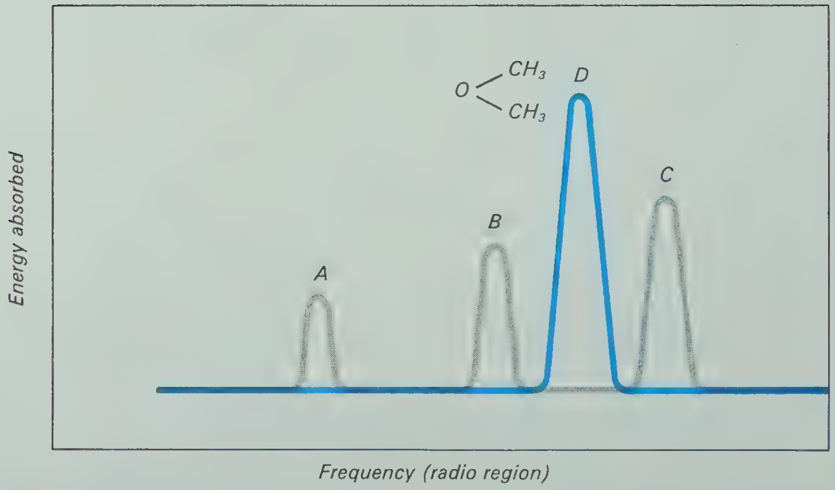


FIGURE 16-13

NMR spectrum of dimethyl ether compared to that of ethanol.

16-7 Review

Chemical analysis leads to the *empirical formula* for a substance. Determination of the molar mass then allows a chemist to write a *molecular formula.* The establishment of the *structural formula* may be a very difficult problem.

Chemists have developed many methods to help them determine the structure of molecules. For years an interpretation of the chemical and physical properties of the substance provided the only route to finding its structure. That chemists were able to unravel the structures of molecules as complex as sucrose and hemin (see pages 373 and 405) testifies to their ingenuity and skill.

Within the past few decades, a number of physical methods to find the structure of molecules have been developed. These methods often depend on how the substance interacts with energy. In this chapter, X-ray diffraction, infrared spectroscopy, and nuclear magnetic resonance have been used to illustrate the physical methods of determining molecular structure.

Questions and Problems for Chapter 16

1

What information is revealed by the empirical formula? The molecular formula? The structural formula? Demonstrate, using propane, C_3H_8.

2

A 100 mg sample of a compound containing only C, H, and O was found by analysis to give 149 mg CO_2 and 45.5 mg H_2O when burned completely. Calculate the empirical formula.

3

When 0.601 gram of a sample having an empirical formula CH_2O was vaporized at 200°C, and one atmosphere pressure, the volume occupied was 388 ml. This same volume was occupied by 0.301 gram of ethane under the same conditions. What is the molecular formula of CH_2O?

One mole of the sample, when reacted with zinc metal, liberated (rather slowly) $\frac{1}{2}$ mole of hydrogen gas. Write the structural formula.

Answer. The molecular formula is $C_2H_4O_2$.

4

Butane has the molecular formula C_4H_{10}. Draw two different ways of arranging these 14 atoms. Remember carbon usually forms four bonds and hydrogen one.

5

Draw the structural formulas for all the $C_2H_3Cl_3$ compounds.

6

Draw the structures of two isomeric compounds corresponding to the empirical formula C_3H_8O.

7

Draw the structural formulas of the isomers of butyl chloride, C_4H_9Cl.

8

What angle would you expect to be formed by the C, O, H nuclei in an alcohol molecule? Explain.

9

It is possible to obtain from 6.1 g of the sweetener, saccharin, 10.3 g CO_2, 1.50 g H_2O, 1.53 g NO_2, and 2.13 g SO_2. What is its empirical formula?

10

Burning 0.600 g of an alcohol obtained by processing petroleum gave 1.32 g CO_2 and 0.72 g H_2O. One mole of the alcohol weighs 60 grams. Determine the molecular and structural formulas. Are there two isomers of this alcohol?

11

When 0.01 mole of an organic acid is dissolved in distilled water and titrated to phenolphthalein endpoint using 0.1 *M* NaOH solution, 200 ml of base solution was needed. How many ionizable hydrogen atoms are there in each molecule?

12

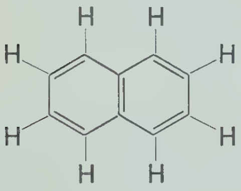
Methyl sulfide, $H_3C—S—CH_3$, and ethyl mercaptan, CH_3CH_2SH, absorb light at different frequencies. Explain.

13

An isomer of the compound C_4H_9O absorbs strongly at 9.5×10^{13} cycles/sec. Is this isomer an alcohol or an ether?

14

The following colorless solids all melt at 79–80°C. Indicate the types of bonds present in each (C—H, etc.) and describe how infrared spectra could be used to identify the compounds.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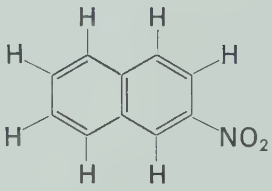
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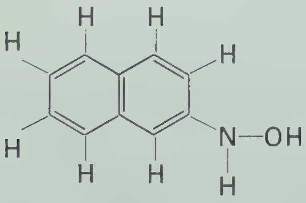

III

15

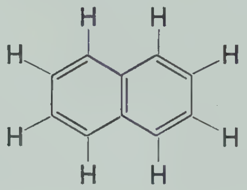
Draw a schematic NMR spectrum for methyl amine, CH_3NH_2.

16

How many peaks do you predict for the NMR spectrum of acetic acid? Explain.

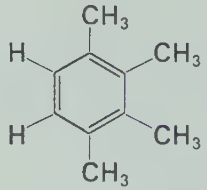
17

Draw a schematic NMR spectrum for naphthalene



18

Draw a schematic NMR spectrum for 1,2,3,4-tetramethylbenzene



19

Compare the formulas of ethyl and tribromoethyl alcohols. Indicate how their NMR spectra would be different. Use Figure 16-12.

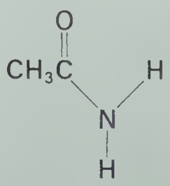
CH_3CH_2OH	CBr_3CH_2OH
ethyl alcohol	tribromoethyl alcohol

20

The NMR spectrum for hypophosphorous acid, H_3PO_2, shows two peaks. The spectrum for phosphoric acid, H_3PO_4, gives only one peak. Explain.

21

Three colorless compounds, all melting in the range 79–81°C, possess the following structures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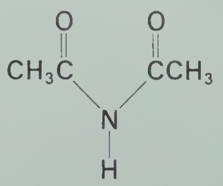
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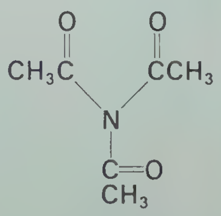
III

Indicate, using schematic spectra, how NMR could help identify them.

Chemical Bonding in Gases, Liquids, and Solids

17

The nature of the chemical bond was discussed in Chapter 10. Although it was convenient to introduce the two words *covalent* and *ionic* in describing chemical bonding, the formation of any chemical bond has only one cause. When electrons are simultaneously attracted by two nuclei, a state of lower potential energy is achieved and a chemical bond forms. In this chapter bonding will receive more detailed study and will be extended to show that the shapes of molecules can be explained qualitatively using the orbital view of atomic structure. You will find it helpful to read Sections 10-1 and 10-2 again before continuing with this chapter.

MOLECULES IN THE GAS PHASE

17-1 Polar Molecules

The fluorine molecule is stable because the potential energy is decreased when a pair of electrons is placed near the two fluorine nuclei. The electrons move about in the molecule so that, on the average, they are distributed symmetrically between and around the two nuclei. This distribution is reasonable since the nuclei are identical and attract the bonding electrons equally.

In the gaseous lithium fluoride molecule, the bonding pair of electrons is again placed near the lithium and fluorine nuclei. Now, however, the electrons move so that they spend more time near the fluorine nucleus, on the average, than they do near the lithium nucleus. The fluorine nucleus attracts the bonding electrons more than the lithium nucleus does.

The shifting of negative electric charge towards the fluorine atom in the LiF molecule causes a charge separation. The molecule has an excess of negative electric charge at the fluorine end and a deficiency of negative electric charge at the lithium end. To indicate this charge separation, the Li—F bond is called a **polar bond**. In LiF, the polar bond makes the whole molecule polar and this **polar molecule** is said to have an **electric dipole**.

Table 17-1 summarizes some of the information on bonding that was presented in Chapter 10. The presence or absence of an electric dipole in the gaseous fluoride molecules is indicated in the last column. This information about electric dipoles, derived from experiments, will be important in the discussion of molecular geometry.

TABLE 17-1

Bonding Arrangements and Polar Nature of Second-Row Fluorides

Compound with Fluorine			Electron Configuration				
Formula	Number of Bonds		1*s*	2*s*	2*p*	Orbitals Used in Bonding	Electric Dipole Present in Gaseous Molecule
LiF	1	Li	⊗	⊘	○○○	*s*	yes
BeF_2	2	Be	⊗	⊘	⊘○○	*sp*	no
BF_3	3	B	⊗	⊘	⊘⊘○	sp^2	no
CF_4	4	C	⊗	⊘	⊘⊘⊘	sp^3	no
NF_3	3	N	⊗	⊗	⊘⊘⊘	p^3	yes
OF_2	2	O	⊗	⊗	⊗⊘⊘	p^2	yes
F_2	1	F	⊗	⊗	⊗⊗⊘	*p*	no
—	0	Ne	⊗	⊗	⊗⊗⊗	none	no

17-2 Molecular Architecture: The Shapes of the Second-Row Fluoride Molecules

Lithium fluoride in the gas phase is a linear diatomic molecule. The bond can be described in terms of the overlap of the 2*s* orbital in lithium with the half-filled 2*p* orbital in fluorine. Because of the vacant valence orbitals in LiF, this substance is very reactive and exists as a diatomic species only at high temperatures. Experiments show that LiF(g) has a very large electric dipole, emphasizing the separation of charge in the molecule.

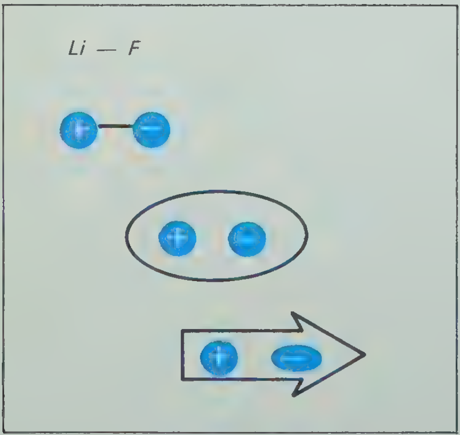

FIGURE 17-1

Representations of the electric dipole in LiF.

The beryllium atom in gaseous BeF_2 uses the 2*s* and one of the 2*p* orbitals in bonding. Just as with the Li—F bond, it is reasonable to expect there would be appreciable charge separation in the Be—F bond. However, electric dipole measurements show *the absence of a molecular dipole* in BeF_2. This result is the clue to the geometry of the beryllium fluoride molecule. There are two Be—F bonds and the electrical properties of the entire molecule depend on how these bonds are oriented relative to each other. To see how charge separation can occur without yielding a polar molecule, we need a method of representing electron shifting. Chemists have several methods, some of which are shown in Figure 17-1. The arrow is the simplest way to depict the charge separation. The arrowhead points to the region of excess negative charge. When an arrow is used for a bond, it indicates a **bond dipole.**

The arrangement of two bond dipoles to give zero molecular dipole is illustrated in Figure 17-2. The molecule must be linear

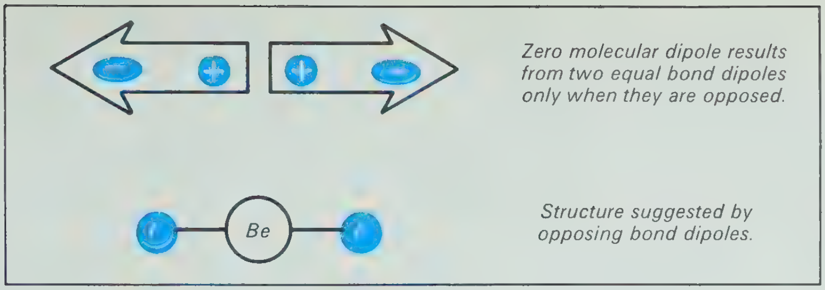
Zero molecular dipole results from two equal bond dipoles only when they are opposed.
Be
Structure suggested by opposing bond dipoles.

FIGURE 17-2

The absence of molecular dipole in BeF_2 suggests a linear molecule.

with the two bond dipoles pointing in opposite directions. This geometry leads to cancellation of the effects caused by charge separation. The bonding in BeF_2 makes use of one *s* and one *p* orbital in beryllium. A linear arrangement of bonds in a molecule is expected when the available bonding orbitals are an *s* and a *p*. Chemists refer to this as **sp bonding.**

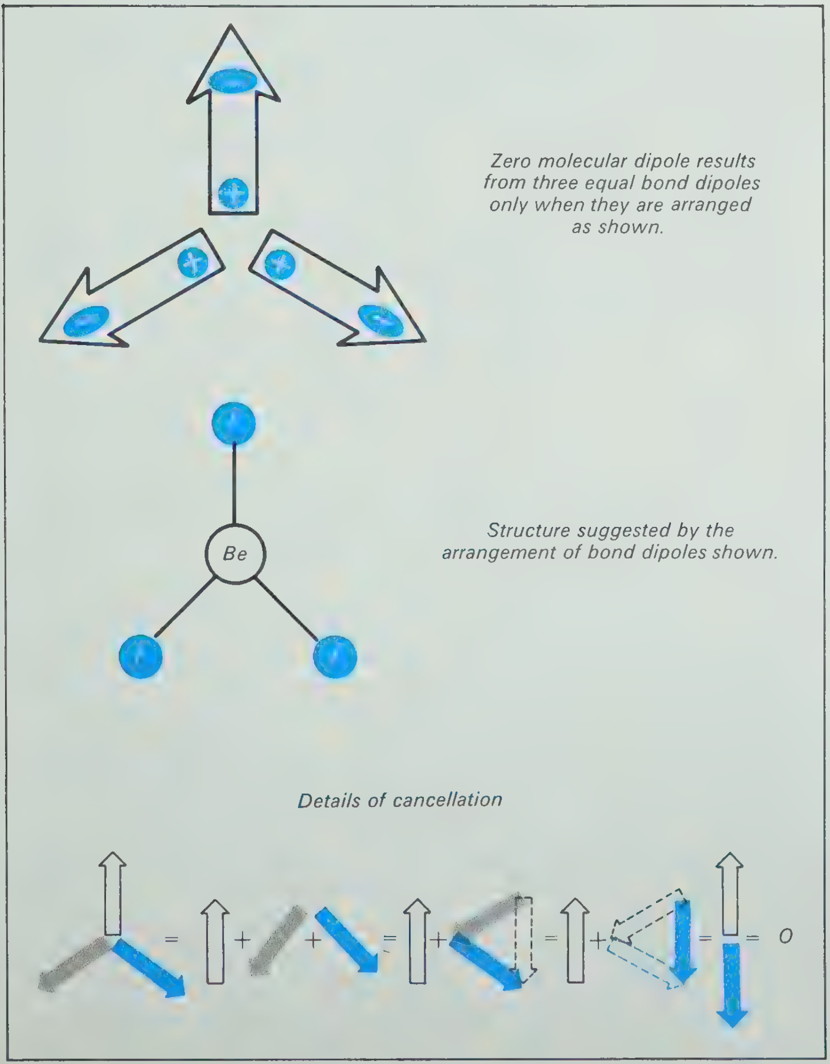
Zero molecular dipole results from three equal bond dipoles only when they are arranged as shown.
Be
Structure suggested by the arrangement of bond dipoles shown.
Details of cancellation
=
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FIGURE 17-3

The absence of molecular dipole in BF_3 suggests a symmetric planar molecule.

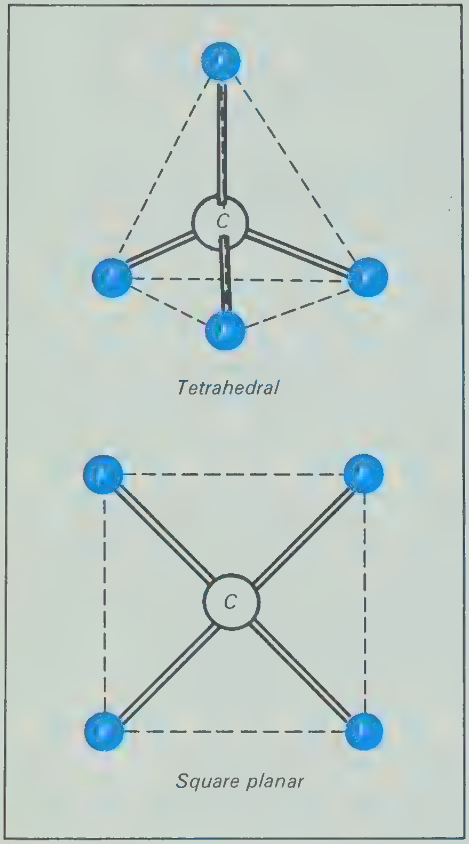


FIGURE 17-4

Two arrangements that would give zero electric dipole for CF_4.

In gaseous BF_3 the boron atom uses the 2*s* and two 2*p* orbitals in bonding. The zero electric dipole found for molecules of BF_3 can be explained by a symmetrical geometry for the three B—F bonds. The only way to achieve this is with the structure shown in Figure 17-3. The boron trifluoride molecule is planar, with the three fluorine atoms at the corners of an equilateral triangle. The lower part of the figure shows the method of deciding the net effect of the arrows. This method is called vector addition. The bonding in BF_3 is called sp^2 (read *s p two*). A planar, triangular arrangement is expected around an atom which uses one *s* and two *p* bonding orbitals.

For carbon, the bonding in CF_4 involves four valence orbitals, the 2*s* and three 2*p* orbitals. The zero value for the molecular dipole of CF_4 can be explained by several different structures. Two of them are shown in Figure 17-4. Additional experiments indicate that carbon compounds have the tetrahedral structure at the left in Figure 17-4. The fluorine atoms occupy the corners of a tetrahedron, with carbon at its center. The angle between any two C—F bonds is the tetrahedral angle, 109° 28′. The bonding in CF_4 is called sp^3 (*s p* three). Tetrahedral geometry is expected around any atom that makes use of one *s* and three *p* orbitals.

EXERCISE 17-1

Molecules that are isoelectronic often have similar molecular geometry. Comment on the bond angles you would expect in the molecules or ions listed. They are isoelectronic with CH_4.

$$NH_3,\ NH_4^+,\ NH_2^-,\ H_2O,\ H_3O^+$$

EXERCISE 17-2

In Exercise 17-1 you suggested a bond angle in NH_3 and H_2O. Compare those with the experimental values of 107° and 105° respectively.

Nitrogen is the next element in the second row. The bonding in its fluoride, NF_3, involves the three 2*p* orbitals of the nitrogen atom. The fact that there *is* a net, or molecular, electric dipole for NF_3 indicates that this molecule *does not* have the symmetrical geometry exhibited by BF_3. Since *p* orbitals are perpendicular to each other, NF_3 might have the structure shown in Figure 17-5. Other experiments confirm this structure. The molecule NF_3 can be thought of as a pyramid, with the nitrogen atom above the triangular base. Approximately 90° bond angles would be expected for the bonding arrangement around any atom using three *p* orbitals. Experiments indicate that the bond angle in NF_3 is about 102°. In NH_3 the bond angles are 107°.

Oxygen difluoride, OF_2, makes use of the two 2*p* orbitals of the oxygen atom to bond to fluorine. The electric dipole for the molecule is not zero. Because of this experimental evidence, the structure of OF_2 *cannot be* linear as BeF_2 is. Other measurements agree with the structure shown in Figure 17-6. One might expect that the F—O—F bond angle would be approximately 90°, the angle between the two 2*p* orbitals of oxygen used in bonding. Experimental measurements give this angle as 103°.

The last molecule to be discussed in this section on elements of the second row is F_2. There is no reason to expect separation of electric charge in this molecule and the measured electric dipole is zero. There is no question of geometry for a diatomic molecule. Bond formation makes use of the last half-filled 2*p* orbital on each fluorine atom.

A summary of this discussion is presented in Table 17-2. The correlation of molecular geometry with the orbitals used in bonding is one of the most helpful regularities that chemists have discovered.

TABLE 17-2

Bonding Orbitals, Bonding Capacity, and Molecular Shape for Row Two Fluorides

Element	Bonding Orbitals	Bonding Capacity	Molecular Shape of the Fluoride	Chemical Formula
He	none	0		He
Li	*s*	1	linear	LiF
Be	*sp*	2	linear	BeF_2
B	sp^2	3	planar, triangular	BF_3
C	sp^3	4	tetrahedral	CF_4
N	p^3	3	pyramidal	NF_3
O	p^2	2	bent	OF_2
F	*p*	1	linear	F_2
Ne	none	0		Ne

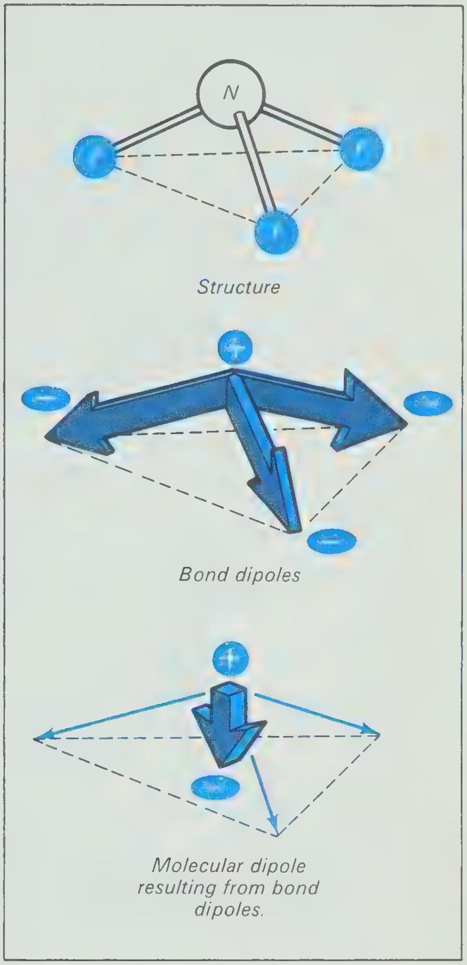


FIGURE 17-5

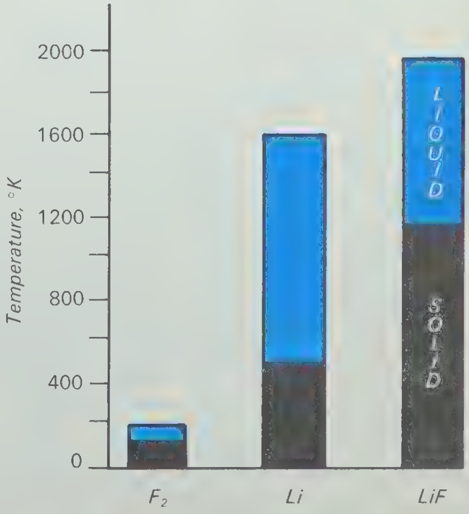
Structure and molecular dipole in NF_3.

THE BONDING IN LIQUIDS AND SOLIDS

In discussing the structure of molecules in the gas phase, our attention was focused on the forces *within* molecules. When sufficient energy is removed from any gas it condenses to a liquid. It then forms a solid if enough energy is removed. The forces that bring about formation of liquids and solids are *between* molecules. The temperature at which these phase changes occur varies from one substance to another. Here are three examples.

Lithium fluoride gas at one atmosphere pressure liquefies when the heat of condensation is removed. It becomes liquid at 1949°K. When the temperature is lowered to 1143°K and the heat of crystallization is removed, the liquid forms a crystal made up of ions, Li^+ and F^-.

In contrast, *lithium* gas at this pressure must be cooled to 1609°K before it can form a liquid and this liquid does not solidify until its temperature reaches 459°K. The solid is a white, soft metallic crystal which does not resemble lithium fluoride. The metal contains lithium atoms.



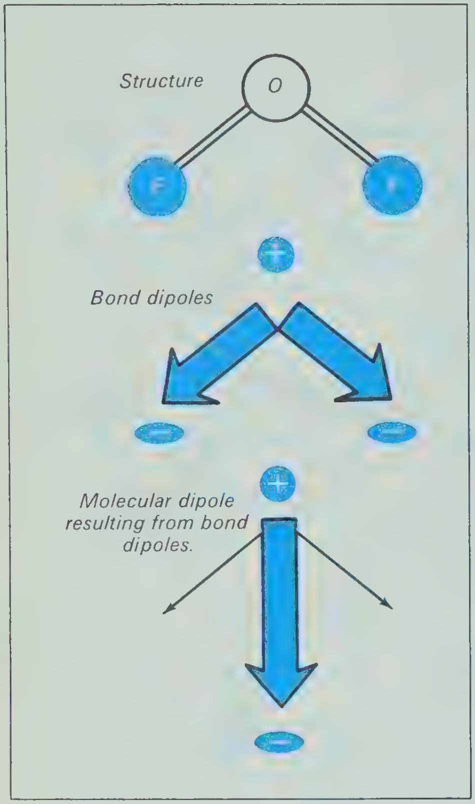


FIGURE 17-6

Structure and molecular dipole in OF_2.

Fluorine gas is equally distinctive. At one atmosphere pressure fluorine must be cooled far below room temperature before liquefaction can occur, at 85°K. The liquid can be solidified to a crystal at 50°K. X-ray studies show that the crystal contains diatomic molecules of F_2.

Why do these three materials behave so differently? Is there some explanation to help us understand these differences? Several times in this book the statement has been made that attractive forces between atoms arise when electrons can be close to two or more nuclei at the same time. This is found to be true in liquids and solids as well as in gases. The three examples above show that the magnitude of the attractive forces in liquids and solids varies greatly, depending on how close electrons can approach these nuclei. This *approach distance* is fixed by the electron occupancy of the valence orbitals. The occupancy of valence orbitals can be used to help predict whether a substance will form a high-melting ionic crystal, a metallic crystal, or a low-melting molecular crystal. In the next sections, explanations for the observed properties will be presented in terms of the molecular structure of solids.

17-3 van der Waals Forces

Polar molecules have relatively strong attraction for each other resulting from the molecular dipoles present. However, even in molecules having no electric dipole, there are attractive forces. For example, two noble gas atoms must attract each other slightly to explain the fact that the noble gases liquefy and form crystalline solids under suitable conditions. These forces are named *van der Waals forces* after the Dutch scientist who studied them. Quantum mechanics helps us understand the origin of these forces. Electron locations inside an atom or molecule are best described by the probability of finding them. For a noble gas, the electron distribution *on the average* is symmetrical. But *at any given instant*, the electron distribution may not be symmetrical. The atom would then have a *momentary electric dipole.* The weak attractive forces in the noble gases arise from interaction between such dipoles.

Atoms of fluorine form diatomic molecules with the formula F_2. In the fluorine molecule, there are enough electrons close to each nucleus to fill the valence orbitals. Under these circumstances, the diatomic molecule behaves like a noble gas toward other fluorine molecules. Momentary dipoles provide a weak attractive force. Molecular fluorine condenses to a liquid at 85°K due to these weak van der Waals forces.

Although charge separation is possible in a compound, there are many substances that do not have appreciable electric dipoles. When all the valence orbitals of such a molecule are filled, giving noble gas electron configurations, then the electrons of a second molecule cannot get very close to the nuclei of the first molecule. The decrease in potential energy is only a few tenths of a kilocalorie per mole when molecules of this sort approach each other. This very weak interaction between molecules is typical of van der Waals forces. It gives rise to low melting solids and low boiling liquids that retain many of the properties of the gaseous molecules.

There are three factors that seem to be important in determining the magnitude of van der Waals forces: the number of electrons, the molecular size, and the molecular shape. These factors can be illustrated with carbon compounds. In Figure 17-7, the melting and boiling temperatures of compounds with the formula CX_4 are shown. (These compounds do not have an electric dipole.) The horizontal axis shows the Periodic Table row number for the outermost atoms in the molecule. These are the atoms which "rub shoulders" with neighboring molecules. As far as van der Waals interactions are concerned, the number of electrons on the outermost atoms is most important in fixing intermolecular forces.

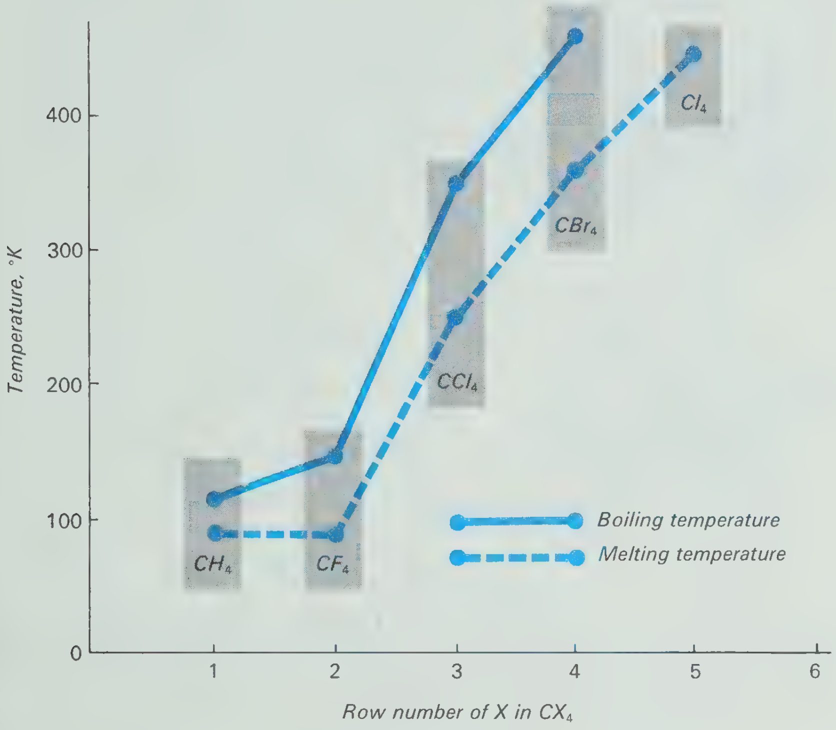
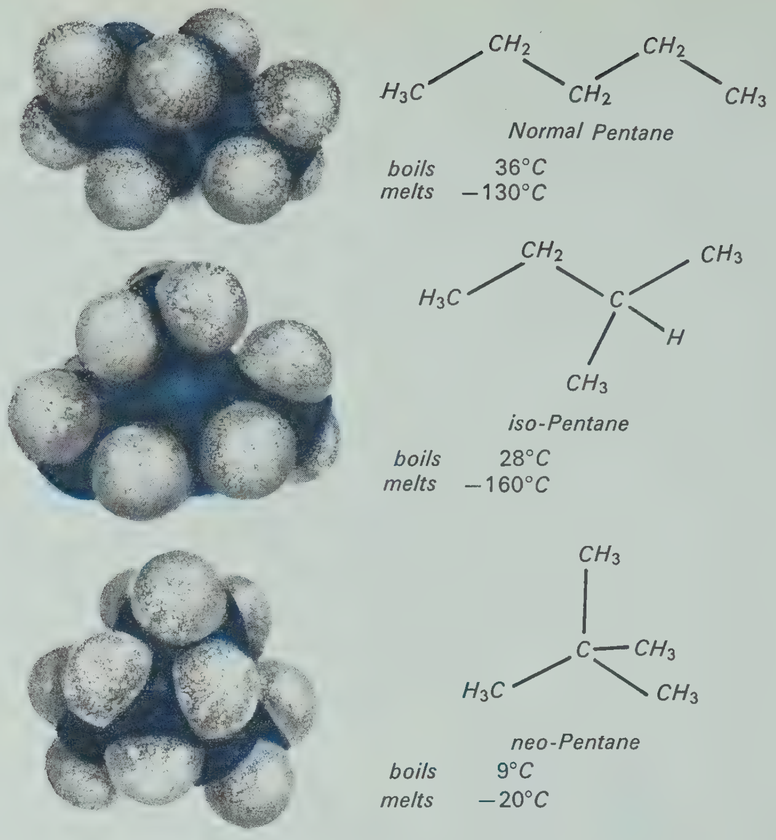


FIGURE 17-7

Melting and boiling temperatures of carbon-halogen compounds, CX_4.

The other two factors are closely related to each other. As the size of a molecule increases, its contact surface increases. The trend in boiling temperature for the hydrocarbon molecules listed in Table 17-3 serves to illustrate this factor. Molecular shape sometimes determines the number of electrons that are "exposed" to other molecules. Notice the three isomers of pentane in Figure 17-8. (Chapter 10, p. 181, has some discussion of isomers.) The extended molecule, *n*-pentane, has a zigzag shape. The van der Waals forces between the external envelope of *n*-pentane molecules would lead to a relatively high boiling temperature. By contrast, the highly


H_3C
CH_2
CH_2
CH_2
CH_3
Normal Pentane
CH_2
CH_3
H_3C
C
H
CH_3
iso-Pentane
CH_3
C
CH_3
H_3C
CH_3
neo-Pentane

boils 36°C
melts −130°C

boils 28°C
melts −160°C

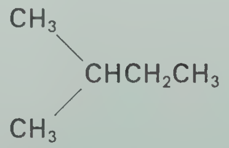
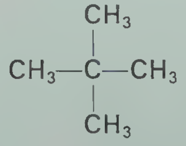
boils 9°C
melts −20°C

FIGURE 17-8
The isomers of pentane.

compact and symmetrical shape for *neo*-pentane offers much less surface contact with its neighbors. Lower van der Waals interaction and therefore lower boiling temperature are expected.

TABLE 17-3

The Boiling Temperature of Some Hydrocarbons

Compound	Formula	Boiling Temperature, °C
Methane	CH_4	−161.5
Ethane	CH_3CH_3	−88.6
Propane	$CH_3CH_2CH_3$	−42.1
n-Butane	$CH_3CH_2CH_2CH_3$	−0.5
n-Pentane	$CH_3CH_2CH_2CH_2CH_3$	36.1
iso-Pentane	 $(CH_3)_2CHCH_2CH_3$	27.9
neo-Pentane	 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$	9.5

17-4 Molecular Solids: Argon, Chlorine, Sulfur, and Phosphorus

Argon, chlorine, sulfur, and phosphorus form molecular solids, with only van der Waals forces acting between the molecules. Argon molecules consist of the single atom. Chlorine forms the diatomic molecule, Cl_2. The electron configuration of the chlorine atom provides a satisfactory explanation for the molecular form of this element. The single half-filled 3*p* orbital can be used to form one covalent bond.

In sulfur, the electron configuration in the valence orbitals suggests that each sulfur atom will form covalent bonds with two other atoms. Sulfur molecules take on the geometrical form of an eight-membered puckered ring. The S_8 molecules have the structure shown in Figure 17-9.

The valence orbitals for phosphorus indicate that each atom should form three covalent bonds to other phosphorus atoms. The geometry around the phosphorus atom is like that around nitrogen in ammonia. Three bonds radiate from each phosphorus atom to form a pyramid with triangular faces. As shown in Figure 17-10, each phosphorus atom makes three bonds in the molecule. The form of phosphorus which is called white phosphorus is made up of individual P_4 molecules, held in the crystal by weak van der Waals forces.

In these four substances, there is strong directional character to the bonds within each molecule. In addition, the valence electrons are closely associated with a particular molecule. When these structural features arise, chemists often speak of *localized electrons.* The van der Waals forces in substances such as these four are nondirectional. Because of this, molecular crystals are usually soft and easily distorted. Two planes of these crystals can move past each other easily because the intermolecular forces are so weak. These substances are very poor conductors of electricity. The electrons are localized, or held, in a particular molecule, with noble gas electron configurations for each atom. Electrons cannot readily move through the crystal because neighboring molecules have filled valence orbitals. Since the molecules do not have an electric charge, there are no charged particles to move and conduct electricity through molecular crystals.

The elements that form molecular crystals are presented in Figure 17-11. These are the elements with high ionization energies. There are many compounds with zero or small electric dipole that form molecular crystals similar to the ones discussed in this section. The large proportion of carbon compounds that will be discussed in Chapter 18 form low melting solids. Each atom in these molecules has a noble gas electron configuration.

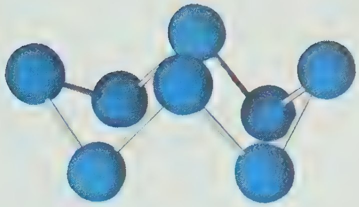


FIGURE 17-9

The structure of S_8.

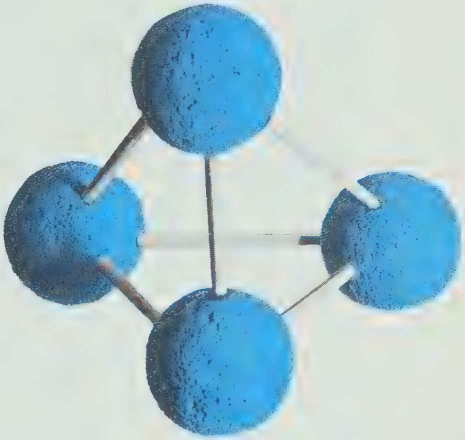


FIGURE 17-10

The structure of P_4.

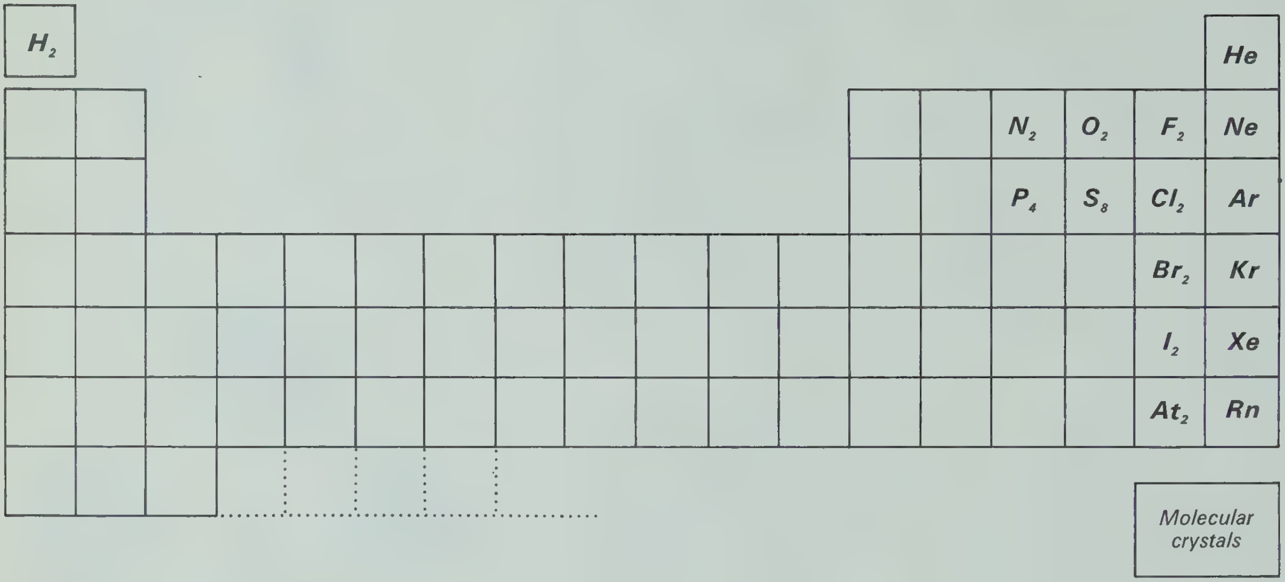


FIGURE 17-11 Elements that solidify as molecular crystals.

EXERCISE 17-3

The compounds ClF and $S_4N_4H_4$ have been synthesized. What would you expect their molecular structures to be? Predict what their melting temperatures might be relative to ice and to salt.

EXERCISE 17-4

Convince yourself that each atom in the three molecules C_2H_6 (ethane), C_2H_4 (ethylene), and C_2H_2 (acetylene) has the electron configuration of a noble gas.

EXERCISE 17-5

In Table 10-7, page 180, there are nine molecules isoelectronic with F_2. Explain why these substances have low melting and boiling temperatures.

17-5 Network Solids: Silicon and Carbon

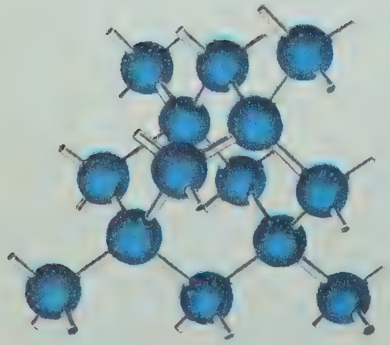


FIGURE 17-12

Silicon, a network crystal.

Silicon has four electrons in the valence orbitals, the 3*s* and the 3*p* orbitals. Silicon tends to form four covalent bonds with tetrahedral geometry around each silicon atom. In the element, each silicon atom is surrounded by and is bonded to four other silicon atoms. This structure is shown in Figure 17-12. It is the same as the diamond structure of carbon. The crystal of silicon can be regarded as a giant three-dimensional molecule. Solids with an extensive web of covalent bonds are called *network solids.* One can readily understand why silicon has a very high melting temperature. A large number of strong covalent bonds must be broken before melting can occur. The hardness and brittle nature of silicon crystals can be explained in terms of this structure. A very large force is required before the crystal will be deformed. The electrical conductivity of silicon is quite low because the electrons are localized in the covalent bonds between the atoms.

Carbon in the form of graphite is another example of a network solid. In contrast to the three-dimensional structure of diamond, graphite has the layered structure shown in Figure 17-13. There are strong covalent bonds between the carbon atoms in any plane. Only weak van der Waals forces exist between the layers, accounting for the ease with which graphite crystals can be cleaved. This property, so apparent from the structure, explains why graphite is useful as a lubricant. The elements which form network solids are indicated in Figure 17-14.

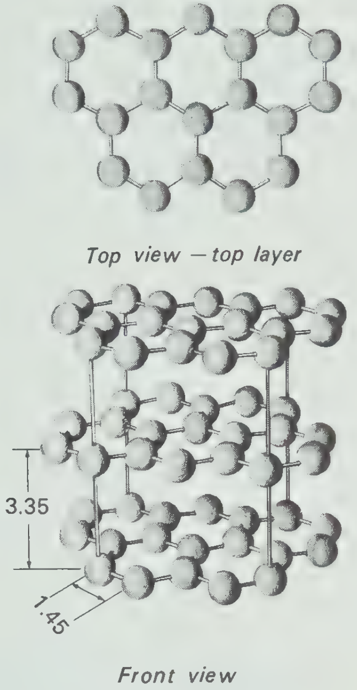


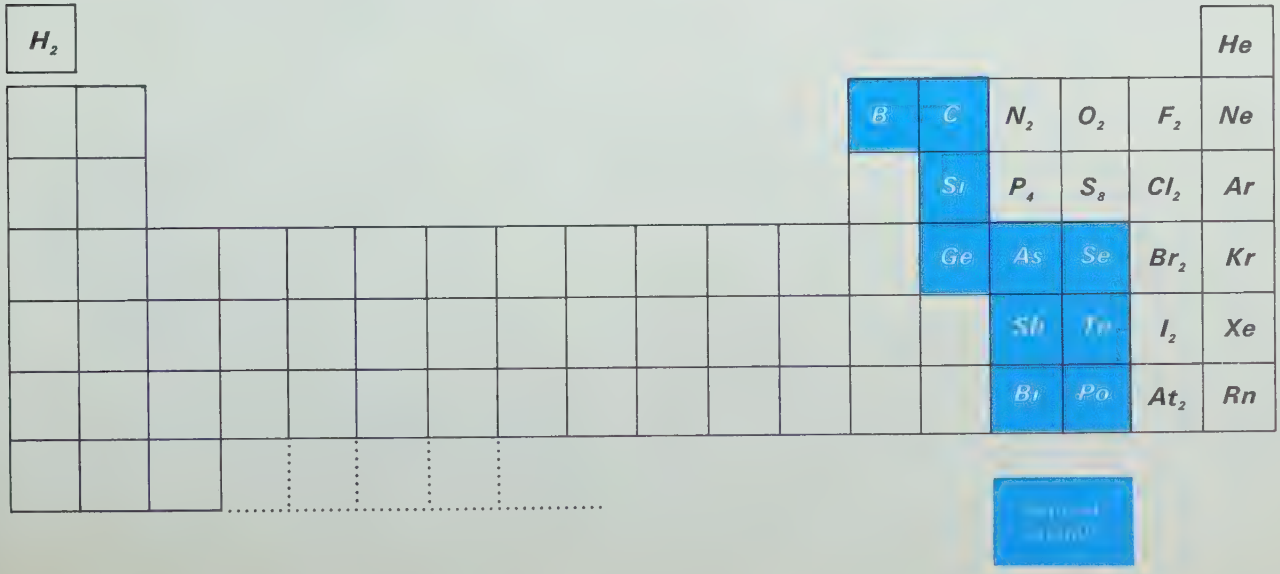
FIGURE 17-13

Structure of graphite.

EXERCISE 17-6

When silica (SiO_2) is heated with carbon, the substance known as carborundum is formed. The empirical formula for carborundum is SiC. This material is important because it is almost as hard as diamond but is much less expensive. What would you expect the structure of SiC to be? How can you account for its hardness?

FIGURE 17-14 Elements that solidify as network crystals.



EXERCISE 17-7

The compound boron nitride, BN, has been known for many years. It has a structure very similar to graphite. Recently, it has been possible to convert this material to the diamond structure, using very high temperatures and pressures. Draw one layer of the graphitelike structure and a portion of the diamond structure for boron nitride.

EXERCISE 17-8

Show that boron nitride and carbon are isoelectronic. Compare the total electronic configuration for one boron atom plus one nitrogen atom with the total electronic configuration for two carbon atoms.

Silica, with the empirical formula SiO_2, is a network solid. Silica and other silicon-oxygen compounds make up about 85% of the earth's crust. Almost all common minerals contain large amounts of silicates, the general term for the silicon-oxygen solids. These are network solids but with interesting and important variations. Three types of network solids are shown schematically in Figure 17-15. Silicon always forms four bonds but in some compounds there are infinite silicon-oxygen-silicon chains; in some there are infinite sheets, with weak van der Waals forces between the layers; and in still others, an infinite three-dimensional structure occurs.

Many properties of the silicates can be understood in terms of the structure at the molecular level. In the one-dimensional chains, the atoms within the chain are strongly linked with covalent bonds, but much weaker forces exist between the chains. This is consistent with the threadlike properties of many of these silicates. The asbestos minerals have this type of structure.

In a similar way the sheets of the two-dimensional silicates are held together by weak forces. These minerals cleave readily into thin but strong sheets. The silicates called micas have this structure. Clays also have this molecular arrangement which accounts for their slipperiness when wet.

The three-dimensional network shown in Figure 17-15 occurs in silica or quartz. Like silicon and carbon, quartz has a very high melting temperature and is one of the hardest substances known. The various minerals in granite have three-dimensional network structures.

17-6 Metallic Solids: Aluminum, Magnesium, and Sodium

The remaining elements of the third row are classed as metals. Their properties are strikingly different from those of the other elements in this row. All metals have high luster or reflectivity. Metals are good conductors of heat and electricity. They can be drawn into thin wires or hammered into very thin sheets without breaking. These properties suggest that the electron configurations of all metals have something in common.

Structural determinations show that each atom in aluminum or magnesium has twelve neighboring atoms. In sodium, each atom has eight neighboring atoms. This is a strange situation! From argon to silicon, the number of covalent bonds in the elements changes from 0 to 4. These numbers are in agreement with the numbers of vacancies in the valence orbitals.

For sodium there is one valence electron to be shared with eight other sodium atoms in the metal. Each sodium atom has four valence

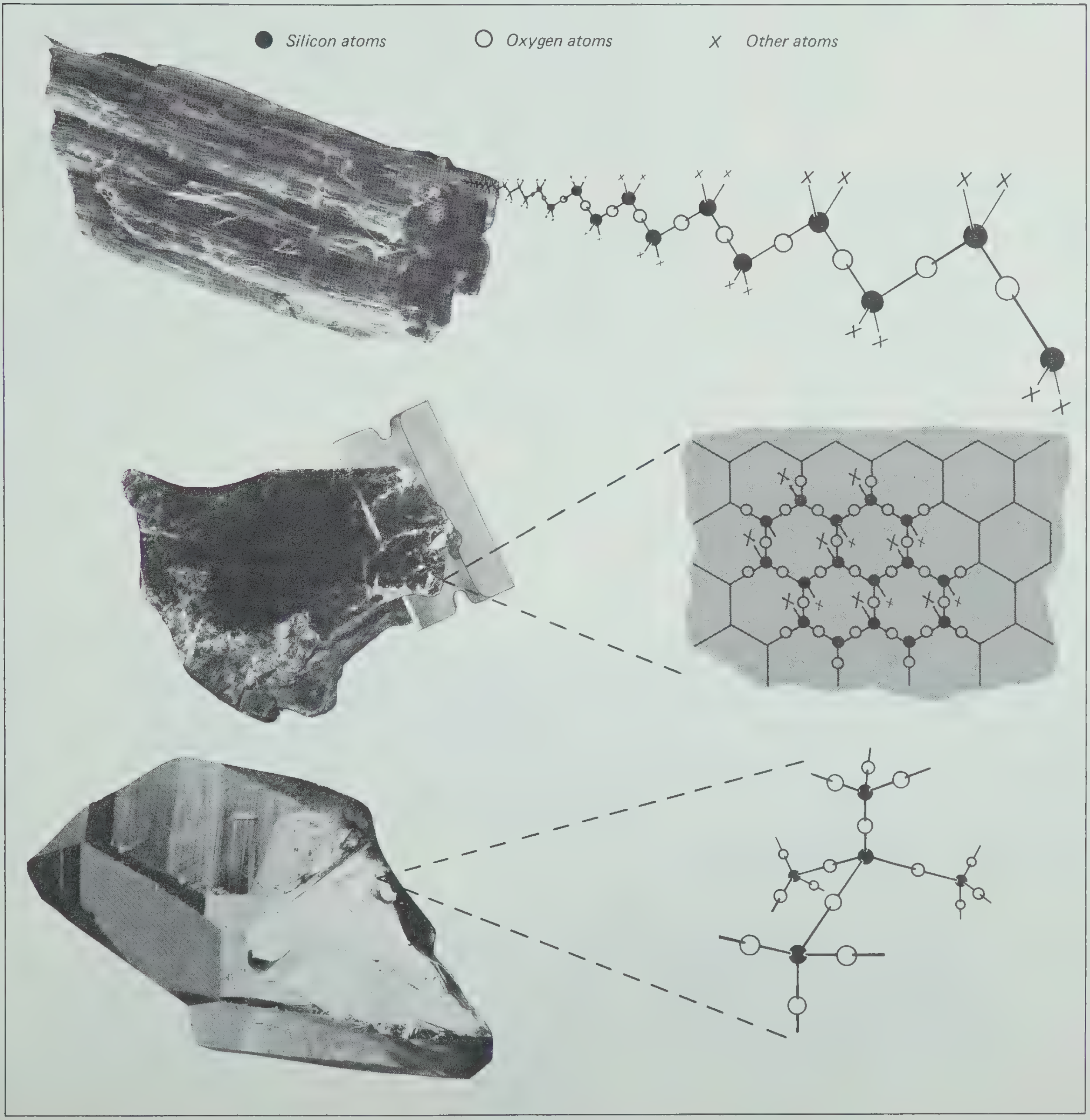


FIGURE 17-15 Silicate structures.

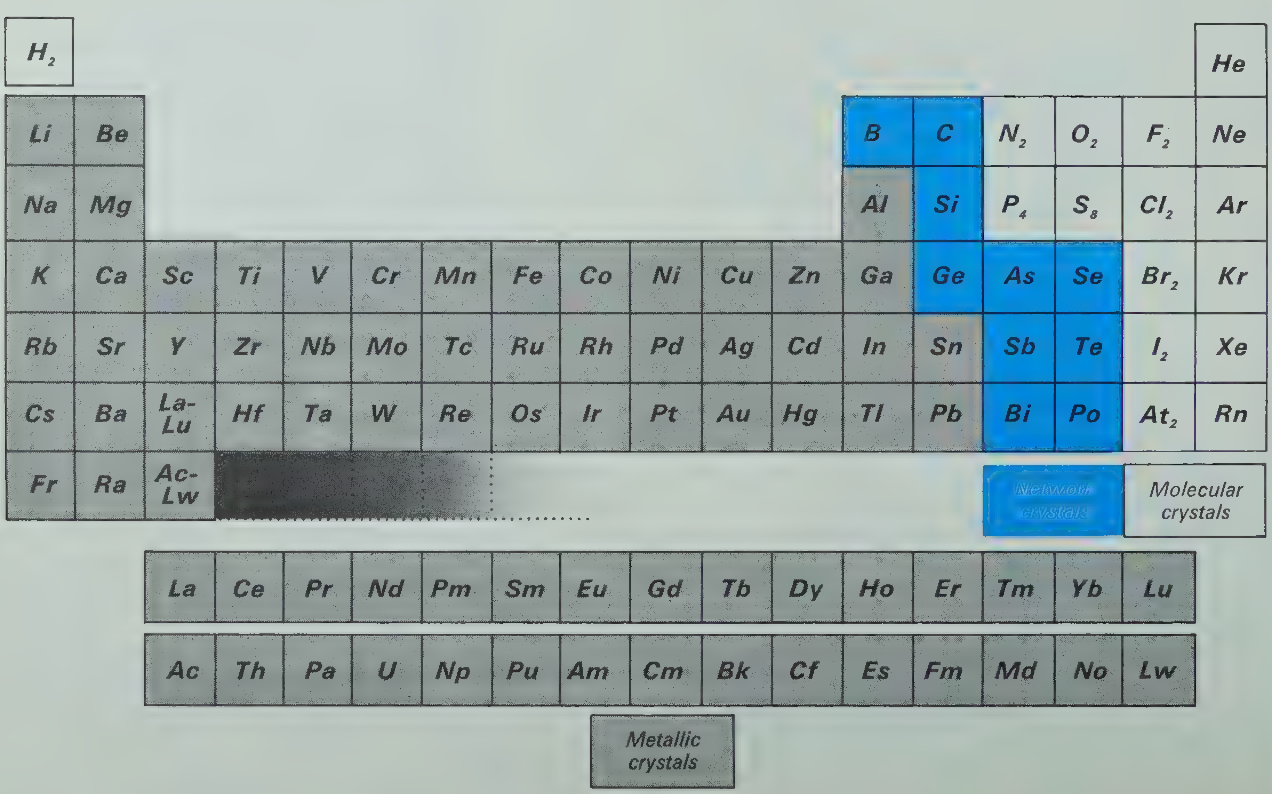
orbitals (one 3*s* and three 3*p*) available for its electron and for the valence electrons of the neighboring sodium atoms. Each atom has an abundance of valence orbitals but a shortage of bonding electrons. The valence electron is free to move in the valence orbitals around its parent nucleus. Everywhere the electron moves, it finds itself between two or more positive nuclei.

What is the nature of the metallic bond? This bond, like all others, forms because the electrons can move in such a way that they are simultaneously near two or more positive nuclei. The space around an atom in a metal is a region of almost uniformly low potential energy. Under these circumstances, it is not surprising that an electron can move easily from place to place. Each valence electron is virtually free to make its way throughout the crystal.

A metal is pictured as an array of positive ions located at the crystal lattice sites, immersed in a "sea" of mobile electrons. The idea of a more or less uniform sea emphasizes an important difference between metallic and covalent bonding. In covalent bonds the electrons are localized in a way that fixes the positions of the atoms quite rigidly. In contrast, the valence electrons in a metal are spread throughout the crystal. Chemists talk about *nonlocalized electrons* in a metal.

The location of the metals in the Periodic Table is shown in Figure 17-16. The metals are found on the left side of the table while the nonmetals are on the right. Furthermore, the elements

FIGURE 17-16 Periodic Table showing crystal types in which elements solidify.


H_2 He
Li Be B C N_2 O_2 F_2 Ne
Na Mg Al Si P_4 S_8 Cl_2 Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br_2 Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I_2 Xe
Cs Ba La-Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At_2 Rn
Fr Ra Ac-Lw
Network crystals
Molecular crystals
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw
Metallic crystals

on the left side of the table have relatively low ionization energies. The low ionization energies of the metallic elements aid in explaining many of the features of metallic behavior.

17-7 Crystal Structure of Metals

There are many ways in which atoms can be arranged in repeating units to form crystals of the elements. In a crystalline solid where all atoms are identical, the state of minimum energy is often achieved when atoms are packed together as efficiently as possible. This condition is referred to as *closest-packing.* Most metals form crystals with a closest-packed structure.

In Figure 17-17, closest-packing in two dimensions is shown. Each atom, represented by the sphere, is surrounded by and is in contact with six other spheres. These are called *nearest neighbors.* (The wax honeycomb in a beehive is very similar in appearance, with hexagons rather than spheres packed together.) To help you keep track of different layers, these spheres are colored gray. There are holes between the spheres.

A second closest-packed layer can be placed on top of the first. The most compact arrangement places the second group of spheres in one of the two sets of holes in the first layer. This is illustrated in Figure 17-18 in which the second layer is blue. Now you can notice two types of openings in the second layer. Some are white because they are over holes in layer one. Some are gray; they are over spheres in layer one. A third closest-packed layer can be placed

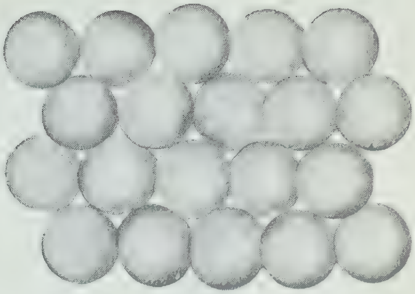


FIGURE 17-17

A layer of close-packed spheres.

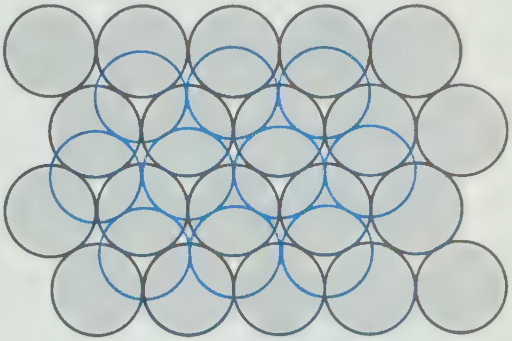
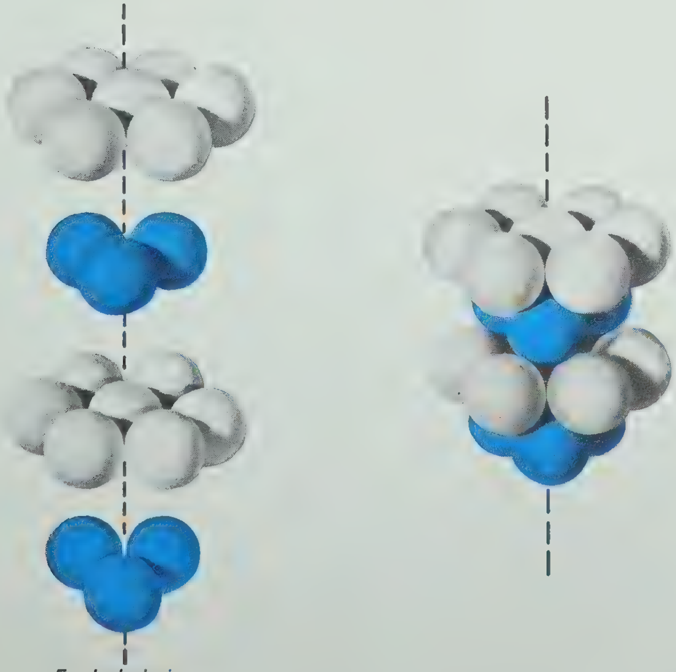


FIGURE 17-18

Two layers of close-packed spheres.



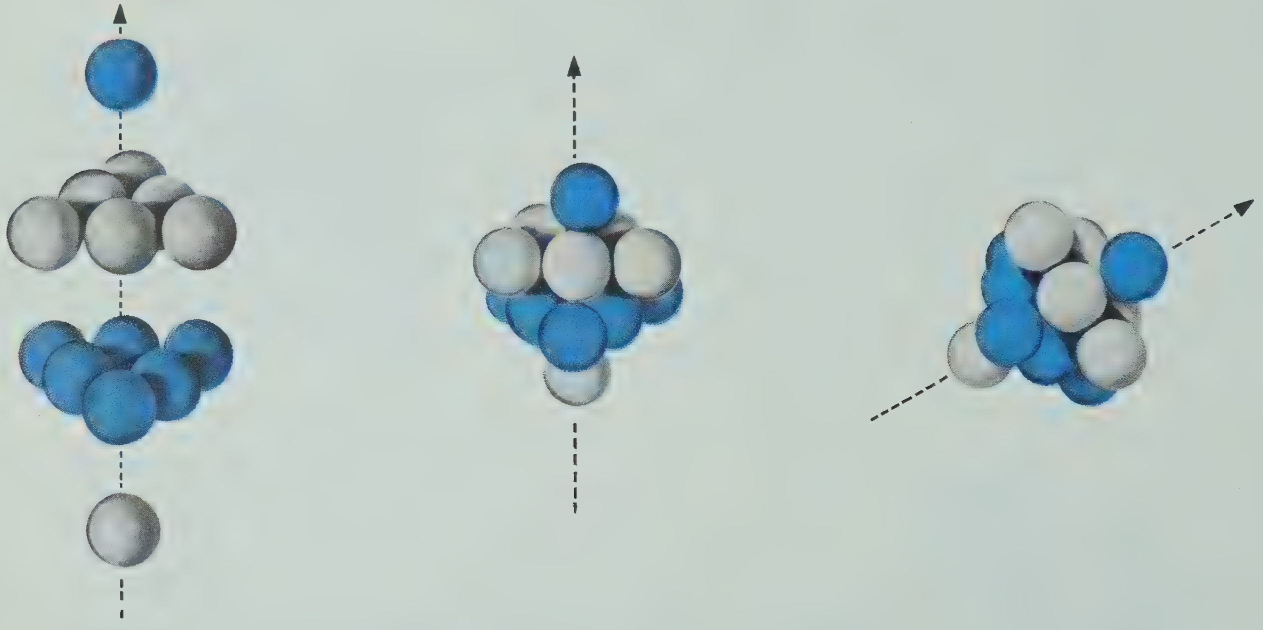
Exploded view

FIGURE 17-19

Hexagonal closest-packing of spheres.

in two ways, either above the original set of spheres in layer one (over the "gray" holes) or above the alternate set of "white" holes. The first possibility is illustrated in Figure 17-19. This pattern of layers, numbered 12121212 . . . , is called the *hexagonal closest-packed structure.* The other arrangement is illustrated in Figure 17-20. Here, the number pattern, 123123 . . . , emphasizes the placement of the layers. This structure is called *cubic closest-packed.* Rotation of the grouping in Figure 17-20 brings out the cubic structure, accounting for the name. There are spheres at the eight corners of the cube and a sphere at the center of each face. This is one of the most important crystal structures. It is often referred to by the name *face-centered cubic.*

FIGURE 17-20 Cubic closest-packing of spheres.



Exploded view

In either of the closest-packed arrangements, each sphere is in contact with twelve other spheres. This is easy to see in Figure 17-19, where a sphere labeled "1" would have six spheres surrounding it in a plane, with three spheres above it and three spheres below it. Solids whose molecules or atoms are approximately spherical and are linked by nondirectional bonds often crystallize with one of the closest-packed structures. The noble gases form crystals with either cubic or hexagonal closest-packing. The hydrogen halides and molecular hydrogen are very nearly spherical molecules. These substances crystallize in one of the closest-packed structures.

In metallic magnesium and aluminum, each atom has twelve nearest neighbors. X-ray studies show that magnesium metal exhibits hexagonal closest-packing and aluminum metal crystallizes in the cubic closest-packing structure. What about sodium metal? Each atom has eight nearest neighbors. Sodium must crystallize in some other pattern than the hexagonal and cubic closest-packed structures.

The crystal structure for metallic sodium is shown in Figure 17-21. There are eight sodium atoms at the corners of a cube and one more in the center. This structure has been given the name *body-centered cubic.* The efficiency of packing atoms in this crystal pattern is slightly less than the two closest-packed forms. A number of metals, including iron and the alkali metals, exhibit body-centered cubic structures at room temperature.

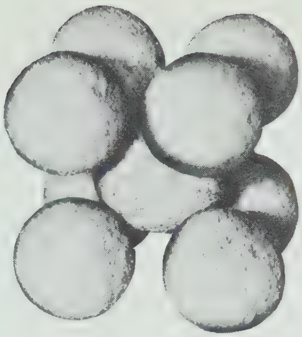


FIGURE 17-21

Body-centered cubic packing of spheres.

EXERCISE 17-9

In Figure 16-8, page 321, the X-ray patterns for aluminum, copper, and sodium metal are shown. What type of crystal structure would you expect for copper?

17-8 An Explanation for Metallic Properties

Nonlocalized or mobile electrons account for many unique features of metals. Since metallic bonds do not have strong directional character, it is not surprising that most metals are soft and can be easily deformed into thin foils and very fine wire without shattering the crystals. Under the influence of a stress, one plane of atoms may slip by another. As this occurs, the electrons maintain some degree of bonding between the two planes. Figure 17-22 illustrates what happens. Metals can often be hardened by adding small amounts of carbon or nitrogen or sulfur. These elements have the property of forming directed covalent bonds. As a result, much more energy is required to move one plane of atoms past another, accounting for the increase in hardness. At the same time, the brittleness of the metal is increased when these elements are added, even in small amounts. The fracture of the crystal may occur when the covalent bonds are broken.

Metals are good conductors of electricity and heat because valence electrons are free to move throughout the solid. In regions of high temperature electrons can acquire large amounts of kinetic energy. This energy can be transferred through the crystal rapidly as electrons interact with other free electrons. Metallic bonding occurs when two circumstances arise:

(1) the ionization energy is low and valence electrons are not held strongly;

(2) there are more unfilled valence orbitals than valence electrons.

In contrast, the electrons in covalently bonded solids are localized in the space between a particular pair of atoms. There are essentially no vacant orbitals available. In these unfavorable circumstances, a large amount of energy must be supplied to move electrons. Hence, covalent compounds are poor conductors.

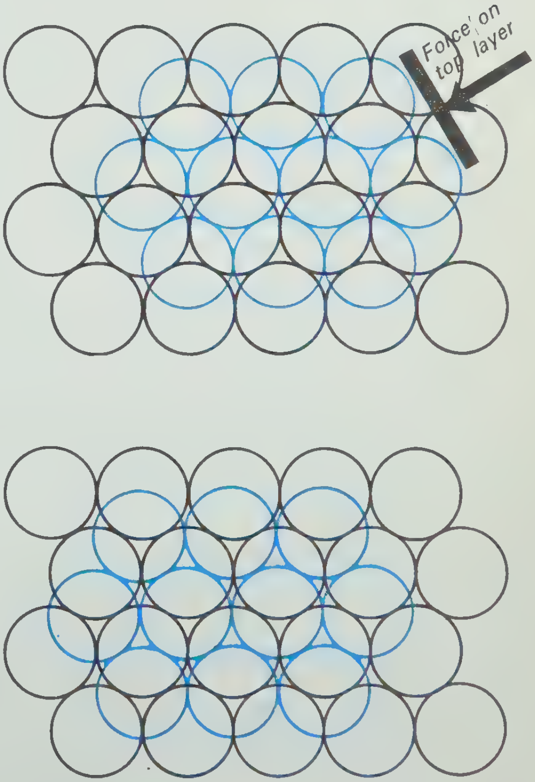


FIGURE 17-22

Atomic view of metal planes sliding over one another.

17-9 Alloys

When two metals are heated above their melting temperatures and then allowed to cool, the solid that is obtained is called an *alloy.* Sometimes an alloy has properties very similar to those of the original metals and, other times, the alloy may have very different properties. Often alloys are more useful than the starting metals. The many kinds of steel that have been developed are examples. Some important alloys are listed in Table 17-4.

TABLE 17-4

Some Useful Alloys

Name	Composition of Alloy (percent by mass)	Uses
Stainless steel	16 Cr 8 Ni 76 Fe	Corrosion resistant steel
Nichrome	60 Ni 15 Cr 25 Fe	Resistance wire in electric heaters and toasters
Alnico	12 Co 10 Al 17 Ni 61 Fe	Permanent magnets
Brass	60–90 Cu 40–10 Zn	
Bronze	80 Cu 15 Sn 5 Zn	Naval hardware
Gold (16 karat)	67 Au 33 Cu	Jewelry
Soft solder	50 Sn 50 Pb	Low melting alloy that bonds to many metals and provides structural and electrical continuity

The tensile strength of iron can be increased tenfold by the addition of small amounts of carbon, nickel, manganese, and other metals. The tensile strength of brass is more than twice that of copper and four times that of zinc. The hardness and strength of alloys can be explained in terms of bonding. The impurity atom may form localized and rigid bonds. Such bonds tend to prevent the slippage of atoms past each other, which results in a loss in malleability and an increase of hardness.

Electrical conductivity in metals apparently depends upon the smooth and uninterrupted movement of electrons through the crystal lattice. Small amounts of impurities in a metal such as copper may seriously affect its ability to conduct electricity. In Section 15-9, page 297, the electrolytic method to purify copper was discussed. The importance of this method is directly related to the gain in electrical conductivity. Table 17-5 shows the conductivity of copper, with various impurities.

TABLE 17-5

Conductivity of Some Copper Alloys

Composition of Alloy (percent by mass)	Temperature °C	Conductivity $(\text{ohm-cm})^{-1}$
100 Cu	25	5.9×10^6
99 Cu 1 Mn	0	2.1×10^6
95.8 Cu 4.2 Mn	25	0.56×10^6
97 Cu 3 Al	0	1.2×10^6
90 Cu 10 Al	0	0.79×10^6
88 Cu 12 Sn	25	0.56×10^6

17-10 Ionic Solids

The most extreme example of charge separation is represented by the formation of ionic solids. In Section 10-1, page 169, the decrease in potential energy as positive and negative ions approached one another to form an ionic lattice was discussed. Each positive ion has only negative ion nearest-neighbors and each negative ion has only positive ion nearest-neighbors.

Earlier in this chapter, the bonding in gaseous lithium fluoride was examined. Although the diatomic molecule is held together because the bonding electrons are near both nuclei, the electron distribution is concentrated toward the fluorine atom. A stable and polar molecule is formed. Stable, but also highly reactive! The valence orbitals of the lithium atom are almost vacant. Lithium fluoride molecules are more stable when each lithium atom, with its vacant valence orbitals, is placed near several fluorine atoms. This is achieved by the formation of a solid. As in metals, an atom with vacant orbitals is more stable when it has several neighbors. There is, however, a significant difference for ionic solids as compared with metals. In lithium fluoride, half of the atoms have high ionization energies. Fluorine atoms hold their electrons tightly. Therefore, the characteristic electron mobility of metals is not present in an ionic solid. The absence of mobile electrons implies that metallic properties are not expected.

Ionic solids form regularly shaped crystals with well-defined crystal faces. Most ionic solids have high melting temperatures because a large amount of energy is needed to overcome the electrostatic forces that hold the crystal together. Ionic crystals cleave along certain directions only. Figure 17-23 suggests cleavage planes in a crystal such as NaCl.

Ionic solids do not conduct electricity because electrons are localized in the vicinity of the negative ions. However, when these

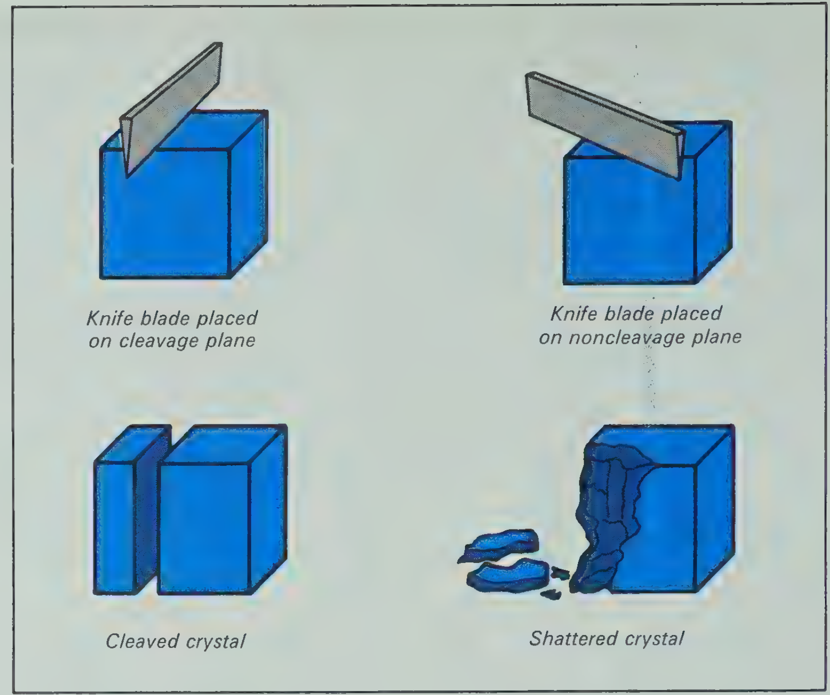

Knife blade placed on cleavage plane
Knife blade placed on noncleavage plane
Cleaved crystal
Shattered crystal

FIGURE 17-23

Cleavage planes in sodium chloride.

solids are melted, the charged ions can move under the influence of an external electric field. The electrical conductivity of molten salts is generally lower than that of a typical metal. It is easy to understand why. In a metal, movement of electrons is responsible for the transport of electric charge. In a molten salt, ionic migration carries electric charge. Since ions have much greater mass than electrons, they move at much lower velocities. The rate at which electric charge is transported by ions is relatively low.

17-11 Structure of Ionic Solids

Ionic solids are found with many different crystal patterns. There is an interesting similarity between some of these structures and the closest-packed structures that were discussed in Section 17-7. In metals where the atoms do not carry an electric charge, atoms often pack together in the most efficient way possible. In an ionic solid such as sodium chloride, ions pack together in the most efficient way, too. There is a new factor arising from the presence of electric charges. Ions of like charge would give rise to large repulsive forces, driving the ions apart. However, the negative ions and the positive ions can alternate and provide attractive forces. The result is shown in Figure 17-24. Positive ions with vacant valence orbitals are surrounded by negative ions with filled valence orbitals and *vice versa*.

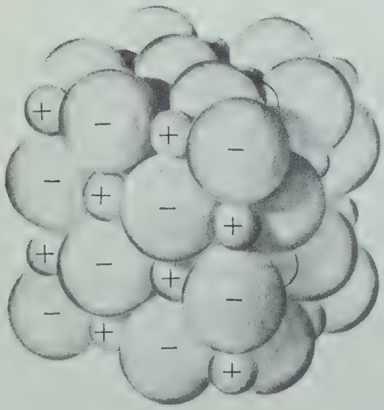


FIGURE 17-24

Close packed ions in a sodium chloride crystal.

17-12 Solubility of Electrolytes in Water

The dissolving of electrolytes in water is one of the most important solvent effects that can be attributed to electric dipoles. Crystalline sodium chloride is quite stable as shown by its high melting temperature. Yet sodium chloride dissolves readily in water. There must be strong interaction between water molecules and the ions formed in solution. This effect can be explained in terms of the polar nature of the interacting substances.

When an electric dipole (as in water molecules) is brought near an ion, the energy is lower if the dipole is oriented to place unlike charges near each other. This process, called *hydration,* is shown in Figure 17-25. In earlier sections of this book, the notation, $Na^+(aq)$, was used to indicate interaction between the solvent water and the sodium ion. The structure of liquid water and of the aquated ions, $H^+(aq)$ and $OH^-(aq)$, are a consequence of the electric dipole of water.

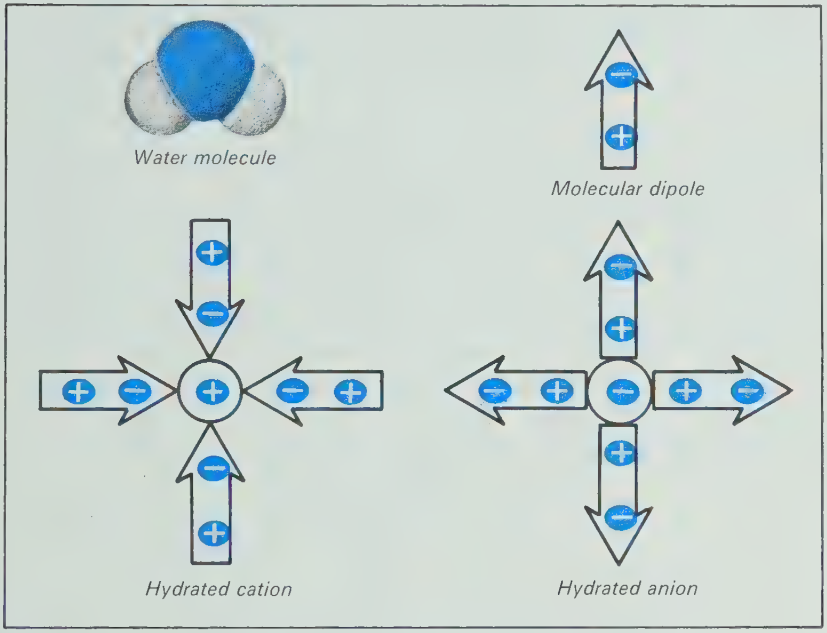


FIGURE 17-25

Hydration of ions.

17-13 The Hydrogen Bond

Section 10-7, page 185, presented some of the observations that led chemists to suggest a hydrogen atom can form two bonds in some compounds. Substances which contain hydrogen attached to oxygen, nitrogen, or fluorine often have abnormally high melting and boiling temperatures. Other properties are also affected, for instance, the infrared and NMR spectra.

The data in Figures 10-6 and 10-7 show that the interaction must be much stronger than van der Waals forces. Experiments show that formation of most hydrogen bonds releases between 3 kcal/mole and 10 kcal/mole:

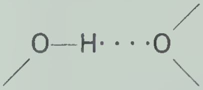
$$\Delta H = -3 \text{ to } -10 \text{ kcal/mole}$$

The energy of this bond places it between van der Waals and covalent bonds. Roughly speaking, the energies are in the ratio

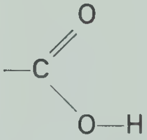
van der Waals attractions : hydrogen bonds : covalent bonds

1 : 10 : 100

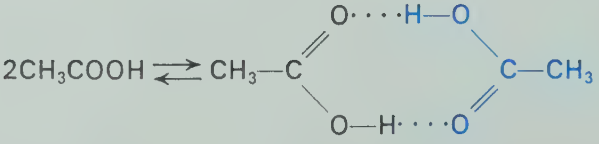
Hydrogen bonds have also been found in solid phases. The most familiar example is solid H_2O, or ice. Ice has a crystal structure in which the oxygen and hydrogen atoms are distributed in a regular hexagonal crystalline lattice that somewhat resembles the diamond lattice (see Figure 17-12). Each oxygen atom is surrounded by four other oxygen atoms in a tetrahedral arrangement. The hydrogen atoms are found on the lines extending between the oxygen atoms.



One of the factors connected with the formation of strong hydrogen bonds is the acidic character of the hydrogen atom involved. Thus the hydrogen bond formed by hydrogen fluoride is one of the strongest known. Acetic acid, CH_3COOH, is a representative of an important class of acidic hydrogen bonding compounds. All of the members of this class possess the structural unit called the **carboxylic acid group:**



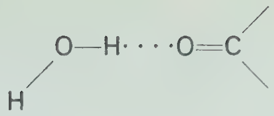
For this type of compound, the formation of hydrogen bonds can lead to the coupling of the molecules in pairs, to form a cyclic structure:



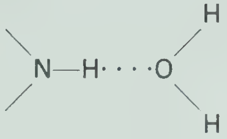
$\Delta H = -14$ kcal

Here the favorable geometrical arrangement with two hydrogen bonds contributes 14 kcal to the stability of the hydrogen bonded product.

Hydrogen bonds play an important part in determining such properties as solubility and phase change temperatures. They affect the form and stability of crystal structures. They play a crucial role in biological systems. For example, water is so common in living matter that it must influence the chemical behavior of many biological molecules, most of which can also form hydrogen bonds. Water can attach itself by hydrogen bonding, either by providing the proton, as in



or in accepting the proton, as in



Furthermore, intramolecular hydrogen bonding is one of the chief factors in determining the structure of such important biological substances as proteins. These substances are discussed in Chapter 18.

17-14 Review

Electrons in a chemical bond may be distributed in a symmetrical fashion between the atoms forming the bond. Whenever two different atoms bond, there is the possibility that electrons will be found more often near one atom than the other. This shift of negative charge gives rise to an electric dipole in the bond. The overall electric dipole for a molecule arises from combination of all the bond dipoles.

The presence or absence of a net electric dipole for the second-row fluorides guides us in understanding the geometrical shapes of simple molecules. The correlation between orbitals used for bonding and the resulting molecular geometry is one of the most useful generalizations chemists have proposed. Here is a summary of the examples discussed in this chapter.

Bonding orbitals used by central atom	Resulting molecular geometry
s	linear
sp	linear
sp^2	planar, triangular
sp^3	tetrahedral
p^3	pyramidal
p^2	bent
p	linear

The bonding *between* molecules, atoms, or ions accounts for the formation of liquids and solids. It has been convenient in this chapter to classify solids under four headings: molecular solids, covalent or network solids, metallic solids, and ionic solids. The melting and boiling temperatures, the physical properties associated with different types of solids, and the electrical conductivity are interpreted in terms of the type of structure in the solid. The significance of *van der Waals forces* in the formation of liquids and solids is presented in this chapter. The hydration of ions in a solvent such as water is outlined as an electrostatic reaction between a dipole (H_2O) and an ion (Na^+ or Cl^-). Hydrogen bonding is also discussed.

Although chemists develop different models and words in talking about the nature of the chemical bond, it is important to state once more the single reason for all atomic and molecular interactions.

> Chemical bonding arises from the decrease in energy that occurs when electrons can interact with two or more nuclei simultaneously.

Questions and Problems for Chapter 17

1

Ethylene, C_2H_4, has zero molecular dipole while hydrazine, N_2H_4, has a large one. Explain. The atoms in each follow normal bonding rules.

2

Would you expect SiH_3F to have a molecular dipole? Explain your answer.

3

Consider the two compounds CH_3CH_3 (ethane) and CH_3NH_2 (methylamine). Why does CH_3NH_2 have an electric dipole while CH_3CH_3 does not?

4

Consider the following series: CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4. In which cases will the molecules have electric dipoles? Support your answer by considering the bonding orbitals of carbon, the molecular shape of the molecules, and the resulting symmetry.

5

Draw the three isomers of dichloroethylene. Which will be polar molecules?

6

Would you expect liquid ammonia to be a good solvent for ionic compounds?

7

Hydrogen peroxide, H_2O_2, has a moderate-sized molecular dipole. Describe the bonding orbitals used and propose a structure to explain the dipole. The atoms in H_2O_2 fit the normal bonding rules.

8

Ozone, O_3, has a molecular dipole. Suggest a structure.

9

Considering comparable oxygen compounds, predict the shape of H_2S and H_2S_2 molecules. What bonding orbitals are used?

10

Predict the type of bonding and the shape of the ion BF_4^-.

11

Predict the structure of the compound N_2F_2 from the electron dot representation of the atoms and the molecule.

12

Sulfur is made up of S_8 molecules; each molecule has a cyclic (crown) structure. Phosphorus contains P_4 molecules; each molecule has a tetrahedral structure.

On the basis of molecular size and shape, which would you expect to have the higher melting point?

13

The elements carbon and silicon form oxides with similar empirical formulas: CO_2 and SiO_2. The former sublimes at −78.5°C and the latter melts at about 1700°C and boils at about 2200°C. From this large difference, propose the types of solids involved. Draw an electron dot or orbital representation of the bonding in CO_2 that is consistent with your answer.

14

Discuss the conduction of heat by copper (a metal) and by glass (a network solid) in terms of the valence orbital occupancy and electron mobility.

15

Contrast the bonds between atoms in metals, in molecular solids, and in network solids in regard to:

(a) bond strength,
(b) orientation in space,
(c) number of orbitals available for bonding.

16

How do you account for the following properties in terms of the structures of the solids?

(a) Graphite and diamond both contain only carbon. Both are high melting yet diamond is very hard while graphite is a soft, greasy solid.
(b) When sodium chloride crystals are shattered, plane surfaces are produced on the fragments.
(c) Silicon carbide (Carborundum) is a very high-melting, hard substance, used as an abrasive.

17

If you were given a sample of a white solid, describe some simple tests you would perform to help you classify the solid as molecular, network, ionic, or metallic.

18

If elements A, D, E, and J have atomic numbers 6, 9, 10, and 11 (in order), write the formula for a substance you would expect to form between the following:

(a) *D* and *J*
(b) *A* and *D*
(c) *D* and *D*
(d) *E* and *E*
(e) *J* and *J*

In each case describe the forces involved between the building blocks in the solid state.

19

Predict the order of increasing melting temperature of these substances containing chlorine: HCl, Cl_2, NaCl, CCl_4. Explain the basis of your prediction.

20

Identify all the types of bonds you would expect to find in each of the following crystals:

(a) argon
(b) water
(c) methane
(d) carbon monoxide
(e) Si
(f) Al
(g) $CaCl_2$
(h) $KClO_3$
(i) NaCl
(j) HCN

21

Aluminum, silicon, and sulfur are close together in the same row of the Periodic Table, yet their electrical conductivities are widely different. Aluminum is a metal; silicon has much lower conductivity and is called a semiconductor; sulfur has such low conductivity it is called an insulator. Explain these differences in terms of valence orbital occupancy.

22

Consider each of the following in the solid state: sodium, germanium, methane, neon, potassium chloride, water. Which would be an example of

(a) a solid held together by van der Waals forces that melts far below room temperature;
(b) a solid with a high degree of electrical conductivity that melts near 100°C;
(c) a high melting, network solid involving covalently bonded atoms;
(d) a nonconducting solid which becomes a good conductor upon melting;
(e) a substance in which hydrogen bonding is pronounced?

23

Each of three bottles on the chemical shelf contains a colorless liquid. The labels have fallen off the bottles. They read as follows.

Label No. 1	Label No. 2	Label No. 3
n-butanol	*n*-pentane	diethyl ether
$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2OCH_2CH_3$
molar mass = 74.12	molar mass = 72.15	molar mass = 74.12

The three bottles are marked *A*, *B*, and *C*, and a series of measurements were made on the three liquids to permit identification. The following data was obtained.

	m.t.	b.t.	density	ΔH vap'n	solubility in water
Liquid *A*	−131.5°C	36.2°C	0.63 g/cc	85 cal/g	0.036 g/100 ml
Liquid *B*	−116	34.6	0.71	89.3	7.5
Liquid *C*	−89.2	117.7	0.81	141	7.9

Which liquid should be given Label No. 1, Label No. 2, Label No. 3? Explain how each type of measurement influenced your choices.

The Chemistry of Carbon Compounds

18

The compounds of carbon furnish one of the most intriguing aspects of chemistry because they play a dominant role in the chemistry of living things, both plant and animal. In addition, there are innumerable carbon compounds useful to man: dyes, drugs, detergents, plastics, perfumes, fibers, fabrics, foods, flavors, and fuels. Manufacture of these compounds has given rise to a huge chemical industry requiring millions of tons of raw materials each year. Where do we find the enormous quantities of carbon and carbon compounds which are needed for this industry? How have chemists been able to transform one carbon compound into another? These are some of the questions considered in this chapter.

18-1 Sources of Carbon Compounds

Coal is a black mineral of vegetable origin. Its production began during prehistoric eras when warm, wet climatic conditions led to rapid growth of plants. As the plants died, they accumulated on the forest floor or in swamps and marshes. The cycles of decay, new growth, and decay caused vast deposits of plant material to build up. Enormous pressures were exerted on the lower levels of this material. In time the layers were pressed into hard beds composed chiefly of the carbon that was present in the original plants. Appreciable amounts of oxygen, hydrogen, nitrogen, and sulfur compounds are also present in coal. When coal is heated to a high temperature *in the absence of air,* it decomposes. Volatile products, coal gas and coal tar, are driven off and a residue called *coke* remains. This valuable industrial material is almost pure carbon. In Chapter 11, the formation of "water gas" from coke was outlined.

About eight gallons of coal tar are distilled from a ton of coal. We speak of coal tar as though it were simple. However, over 200 different carbon compounds have been isolated from it. While the great value of coal to mankind has been as a fuel, the many substances in the gas and tars make coal a very important source of chemical raw materials.

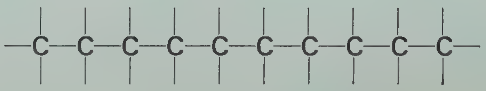
A second source of carbon compounds is petroleum, a complex mixture which may range from a thin, volatile liquid to a viscous, tarry substance. Petroleum also had its origin in living matter that underwent chemical changes over the course of geological time. It is found underground between the grains of sandstone left from ancient seas. Natural gas is found in similar types of rock. Huge oil refineries daily change millions of gallons of crude oil into useful products.

Plants and animals are themselves highly effective chemical factories and they synthesize many other carbon compounds useful to man. These include proteins, sugars, cellulose, starches, vitamins, plant oils, waxes, fats, gelatin, dyes, drugs, and fibers.

Because all of these sources of carbon compounds had their origin in living matter, plant or animal, the chemistry of carbon is called **organic chemistry.** This name came from the belief, now discarded, that living materials were organized in a unique way or contained some special ingredient not present in nonliving matter. Compounds containing carbon are called organic compounds. Some chemists exclude CO_2, CO, and a few ionic substances such as sodium carbonate, Na_2CO_3, and sodium cyanide, NaCN.

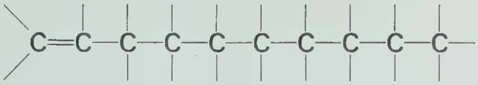
Although each of the sources mentioned accounts for thousands of tons of material, it is interesting that most of the carbon of our planet is not in these forms. It has been estimated that the CO_2 in the earth's atmosphere contains about 40 times as much carbon as in all the fossil fuels and forests. But the largest store of all is the inorganic carbonates in limestone and other minerals. These rocks contain about 400,000 times as much carbon as the coal, oil, and wood reserves. Perhaps future chemists will find an economical way to convert the carbon in such minerals to more useful forms.

There are several million different carbon compounds known. The 100,000 new organic compounds synthesized in just one year exceeds the total number of compounds known that contain no carbon! The number of organic compounds is very large because each carbon atom has an outstanding ability to form highly directed covalent bonds to other carbon atoms. With the formation of many carbon-carbon bonds goes the possibility of having isomers. Thus, each molecular formula can represent many compounds. For example, you learned in Chapter 10, Exercise 10-6, that three compounds have the same formula, C_5H_{12}. It has been found that $C_{10}H_{22}$ represents 75 different compounds and $C_{30}H_{62}$ has about *four billion* distinct arrangements. Another factor producing a large number of compounds is the ability of carbon to form many stable substances with double and triple bonds between the carbon atoms themselves. Picture just one of the 75 forms of decane, $C_{10}H_{22}$,



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

There are five different ways in which two hydrogen atoms could be removed to produce a double bond. One of these is

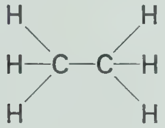


EXERCISE 18-1

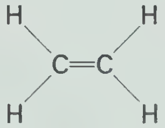
Draw structural formulas for the four other possible isomers of $C_{10}H_{20}$. Why are there not nine?

18-2 Hydrocarbons and Their Reactions

In Chapters 10 and 17, hydrocarbons were used as examples to illustrate covalent bonding and molecular geometry. Ethane, ethylene, and acetylene are examples of hydrocarbons



ethane
C—C single bond



ethylene
C—C double bond

$H-C\equiv C-H$

acetylene
C—C triple bond

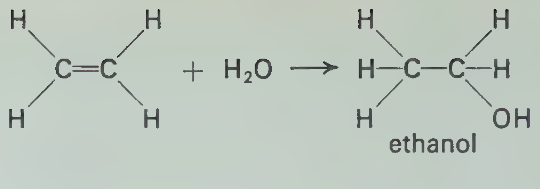
Ethane contains only carbon and hydrogen atoms connected by single bonds. Such compounds are called saturated hydrocarbons. Ethylene and acetylene are unsaturated hydrocarbons. There is a carbon-carbon double bond in ethylene and a triple bond in acetylene.

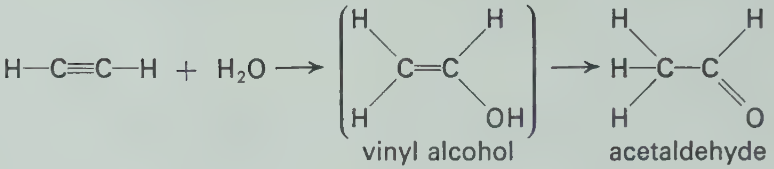
Saturated hydrocarbons are widely used as fuels to heat our homes and to move our automobiles. Therefore it may be surprising to learn that these compounds are not very reactive. They are unreactive to strong acids and bases and to many oxidizing or reducing agents. Under very extreme conditions saturated hydrocarbons undergo oxidation with oxygen or with the halogens. A few reactions with methane can serve as illustrations.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$
$$4\,CH_4 + O_2 \longrightarrow 1\,C_2H_2 + 2\,CO + 4\,H_2$$
$$CH_4 + X_2 \longrightarrow CH_3X, + HX$$

(Further reactions give CH_2X_2, CHX_3, and CX_4.)

These reactions are often difficult to control and mixtures of the products arise. Therefore it is important to transform the saturated hydrocarbons into other substances which are much more reactive. Then we can use synthetic procedures which can be controlled, to make a great variety of useful substances. Ethylene and acetylene, with their multiple carbon-carbon bonds, are much more reactive than ethane. Their reactions with water are important industrial routes to ethyl alcohol and acetaldehyde.





In Chapter 16 the reactions of ethanol were explained on the basis of the behavior of the —OH group in CH_3CH_2OH. For many of the reactions of ethanol, it is the OH group that reacts. The rest of the molecule has the saturated hydrocarbon structure, CH_3CH_2—, which is relatively unreactive. It is helpful to regard ethanol as containing two parts, the C_2H_5— or ethyl group, which is unchanged during many reactions, and the —OH or hydroxyl group, which can change.

Such a division can be made of many organic molecules. There is a good reason to do so. In that way, the millions of compounds can be reduced to a few hundred types according to the reactive group they contain. Those groups that most frequently change during reaction are called **functional groups.** Through study of the chemical behavior of a few alcohols we can learn the main reactions of hundreds of compounds containing the —OH group as the only functional one.

In order to focus attention on the group that is reacting, a simplified formula is used. In it the part of the molecule other than the functional group is represented by **R**. Thus the general formula for **alcohols** is **R—OH**. When the group represented by *R* contains only chains of carbon and hydrogen atoms, it is called an **alkyl** group. The ethyl group, C_2H_5—, is a specific example of an alkyl group.

In Section 16-2 it was mentioned that ethyl bromide forms when ethanol reacts with hydrogen bromide. Similar treatment of ethanol with hydrogen chloride or hydrogen iodide gives the corresponding ethyl halides:

$$CH_3CH_2OH + HCl \longrightarrow CH_3CH_2Cl + H_2O$$
$$CH_3CH_2OH + HI \longrightarrow CH_3CH_2I + H_2O$$

EXERCISE 18-2

Write the equation for the general reaction between alcohols and HCl. Use —R to represent the hydrocarbon part of the molecules.

The hydroxyl group has been displaced, and the halogen atom substituted. The group CH_3CH_2— has not changed. Indeed, this group has appeared in most of our discussion so far. Sometimes it was attached to oxygen, as in ethanol and sodium ethoxide, and sometimes attached to other atoms, as in the ethyl halides. Looking at the structural formula of ethane, you see that it is simply the $CH_3CH_2—$ group attached to hydrogen:

$$CH_3CH_2—H \qquad \text{or} \qquad CH_3CH_3$$

Because ethyl bromide and ethyl alcohol can be thought of as being derived from ethane by the substitution of —Br or —OH for one of its hydrogens, they are called derivatives of ethane. Ethane is the parent hydrocarbon for a series of related compounds, some of which will be discussed in the next section.

EXERCISE 18-3

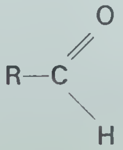
Give the structural formula for two derivatives of propane.

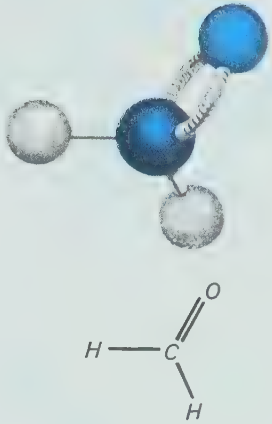
18-3 Oxidation of Organic Compounds

By far the majority of the several million known compounds of carbon also contain hydrogen and oxygen. There are several types of oxygen-containing organic compounds and they can be studied as an oxidation series. For instance, the compound methanol, CH_3OH, is very closely related to methane, as their structural formulas show. Methanol can be regarded as the first step in the complete oxidation of methane to carbon dioxide and water.

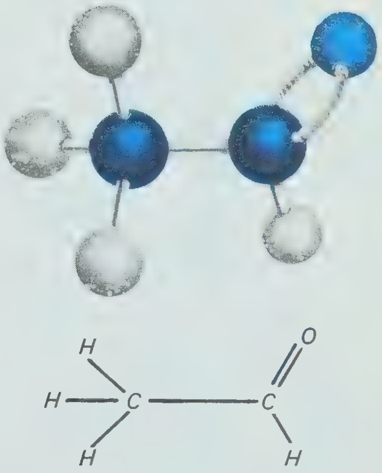
Alcohols react with inorganic oxidizing agents such as potassium dichromate, $K_2Cr_2O_7$. When an acidic solution of potassium dichromate reacts with methanol, the solution turns from bright orange to muddy green, because of the production of green chromic ion, Cr^{3+}. The solution then has a strong odor easily identified as that of formaldehyde, CH_2O. The structure for this compound is shown at the top in Figure 18-1. Notice that the bond between carbon and oxygen has become a double bond. All the atoms in formaldehyde lie in the same plane.

Acetaldehyde can be made from ethanol by the same type of oxidation that yields formaldehyde from methanol. Acetaldehyde contains a methyl group attached to a $>C=O$ portion, called a **carbonyl group.** In this compound the carbonyl group also has a hydrogen atom bonded to it. You might correctly predict that there would be a series of such compounds with different alkyl groups connected to the carbonyl group. There is such a series. The compounds are called **aldehydes** and have the general formula





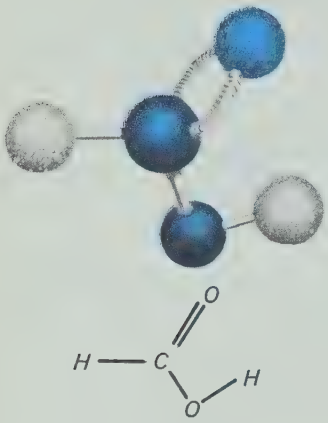
Formaldehyde, HCHO



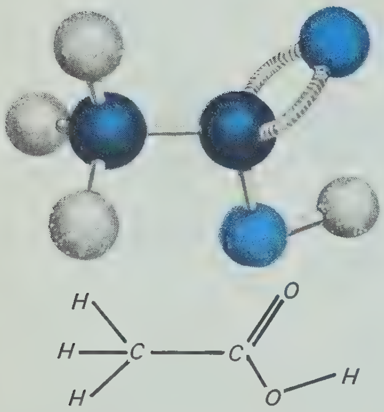
Acetaldehyde, CH_3CHO

FIGURE 18-1

The structure of aldehydes, formaldehyde and acetaldehyde.



Formic acid, HCOOH



Acetic acid, CH_3COOH

FIGURE 18-2

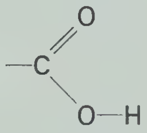
The structure of carboxylic acids, formic and acetic acid.

EXERCISE 18-4

Write the formula of the aldehyde made from normal pentane.

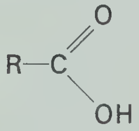
Another oxidation product can be obtained from the reaction of an acidic solution of potassium permanganate with methanol. The product has the formula HCOOH, and is called formic acid. The structural formula of formic acid is shown in Figure 18-2. The structure of formic acid is also related to the structure of formaldehyde. If one of the hydrogen atoms of formaldehyde is replaced by an OH group, the resulting molecule is formic acid.

Just as methanol can be oxidized to formic acid, ethanol can be oxidized to an acid, CH_3COOH, called acetic acid. The molecular structure of acetic acid is also shown in Figure 18-2. The atomic grouping



or —COOH

is called the **carboxyl** group and acids containing this group are called **carboxylic acids.** Their general formula is



or RCOOH

The oxidation of acetic acid is difficult to accomplish. It does not react in solutions of $K_2Cr_2O_7$ or $KMnO_4$. Vigorous treatment, such as burning, causes its complete oxidation to carbon dioxide and water. Formic acid also can be oxidized to carbon dioxide and water by combustion with oxygen.

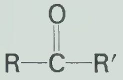
EXERCISE 18-5

Butanol is an alcohol with the structural formula, $CH_3CH_2CH_2CH_2OH$. If it is oxidized carefully, an aldehyde called butyraldehyde is obtained. Vigorous oxidation gives an acid called butyric acid. Draw structural formulas of these compounds like those shown in Figures 18-1 and 18-2.

The series alcohol, aldehyde, carboxylic acid represents the stepwise oxidation path taken when the —OH group in the alcohol is on an end carbon of a chain. There are some alcohols having the —OH group on a carbon atom other than an end one. Figure 18-3 illustrates the series for a three-carbon compound.

When 2-propanol is oxidized, a carbonyl group forms from the hydroxyl group. This is just what happened before. But the product, acetone, has a new feature not present in acetaldehyde. In Figure 18-4 you can see that the carbonyl group in acetone has no hydrogen attached to it. It cannot be oxidized to an acid. It will react with oxygen, giving CO_2 and water as in the oxidation of acetaldehyde or acetic acid.

Acetone is the simplest member of a class of compounds called **ketones.** They are quite similar in structure to the aldehydes, since each contains a carbonyl group. The general formula for ketones is

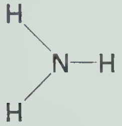


$$R-\overset{O}{\overset{\|}{C}}-R'$$

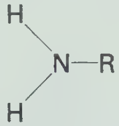
Huge amounts of aldehydes and ketones are used industrially in a variety of chemical processes. Furthermore, these functional groups are important in chemical synthesis of medicines, dyes, plastics, and fabrics.

18-4 Amines (Organic Bases)

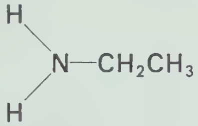
Alcohols can be related to water by imagining that an alkyl group (such as $—CH_3$) has been substituted for one of the two hydrogen atoms of water. In the same way, a group of compounds called amines is related to ammonia:



ammonia



an amine



ethylamine

Amines can be prepared by direct reaction of ammonia with an alkyl halide, such as CH_3Br or CH_3CH_2I. Iodides react with the highest rate.

$$CH_3CH_2I + 2\,NH_3 \longrightarrow CH_3CH_2NH_2 + NH_4I$$

This equation represents a net change that occurs when an excess of ammonia reacts with an alkyl iodide. The mechanism of the reaction is thought to involve two steps. The first is analogous to the attack of the hydroxide ion on an alkyl halide (see Figure 12-14):

$$NH_3 + RI \longrightarrow RNH_3^+ + I^-$$

The second step is a proton transfer reaction:

$$NH_3 + RNH_3^+ \longrightarrow RNH_2 + NH_4^+$$

18-5 Acid Reactions

Oxidation of an aldehyde gives an organic acid. All such acids contain the functional group —COOH, the carboxyl group. The bonding in this group is

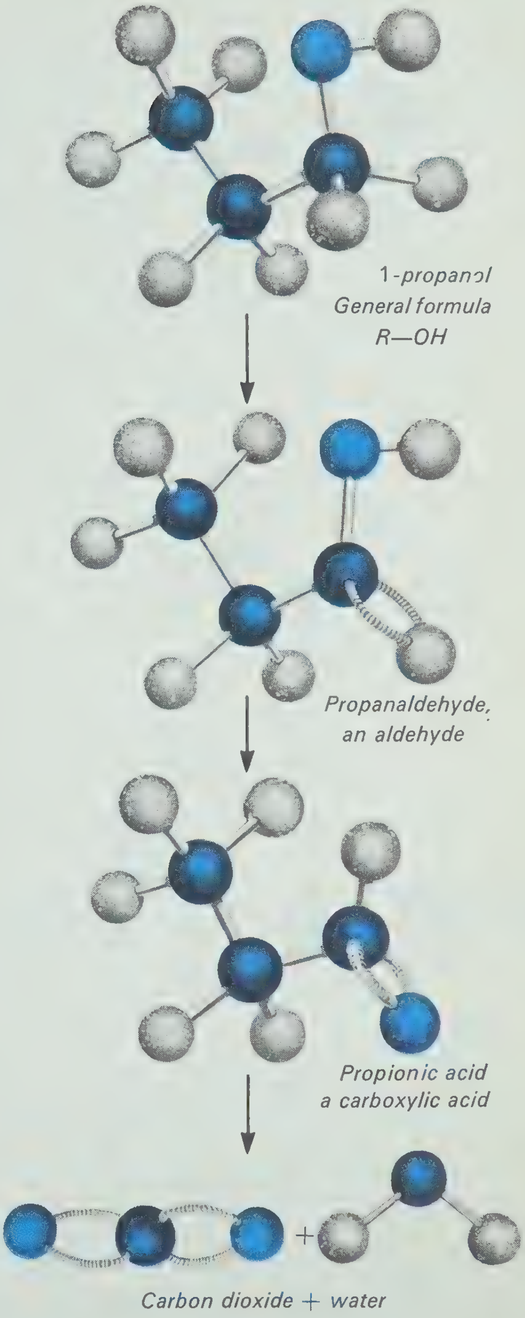


FIGURE 18-3

Successive stages in the oxidation of a normal alcohol, R—OH.

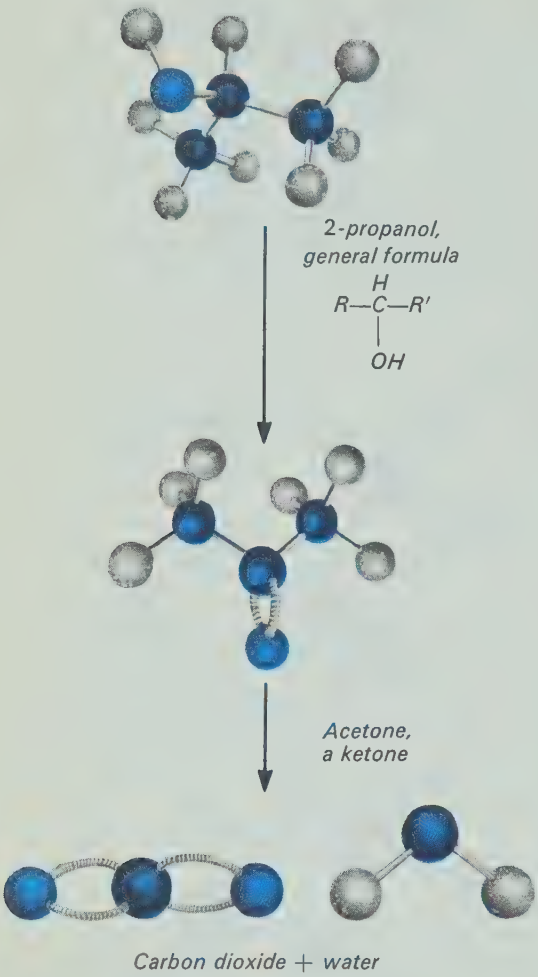
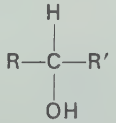
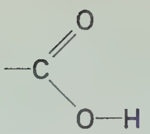

2-propanol,
general formula
H
R—C—R'
OH
Acetone,
a ketone
Carbon dioxide + water

FIGURE 18-4

Successive stages in the oxidation of an alcohol of general formula

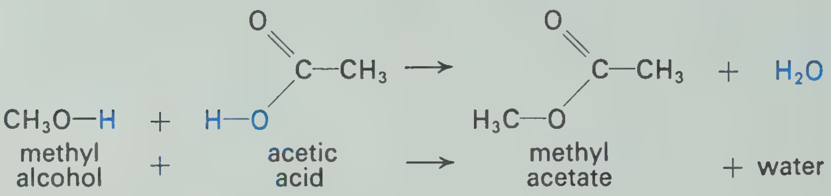

$$R-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-R'$$



The carboxyl group releases a proton, acting as a Bronsted acid.

In addition to this acidic behavior, an important characteristic of carboxylic acids is that the entire OH group can be replaced by other groups. The resulting compounds are called **acid derivatives.** Only two types of acid derivatives, esters and amides, will be considered.

Compounds in which the —OH of an acid is transformed into —OR (such as $—OCH_3$) are called **esters.** They can be prepared by the direct reaction between an alcohol and the acid. For example,

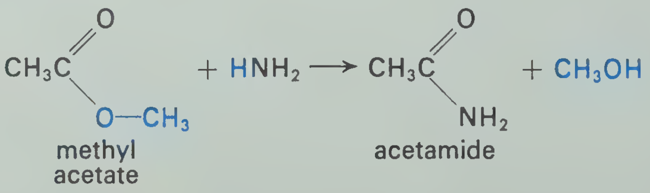

methyl alcohol
+
acetic acid
→
methyl acetate
+ water

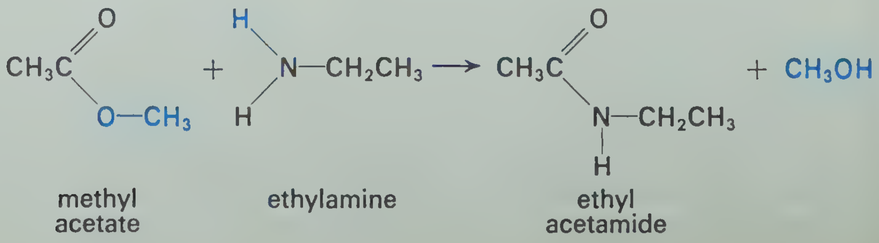
Esters are important substances. The esters of low molar mass have fragrant, fruitlike odors and are used in perfumes and artificial flavorings. Esters are useful solvents. This is the reason they are commonly found in "model airplane dope" and fingernail polish remover.

EXERCISE 18-6

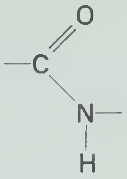
Write equations for the reaction of (a) ethanol and formic acid; (b) propanol and propionic acid; (c) methanol and formic acid. Name the esters produced.

Another class of acid derivatives has been given the name **amides.** Amides are formed when the —OH group of an acid is replaced by an $—NH_2$ group. An amide can be made by reacting ammonia or an amine with an ester.


methyl acetate
acetamide


methyl acetate
ethylamine
ethyl acetamide

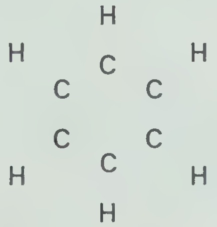
Note the similarity of the two reactions. Amides are of special importance because the amide grouping



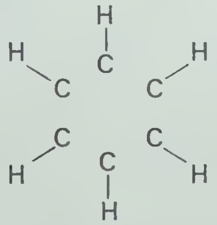
is the basic structural element in the long-chain molecules that make up proteins and enzymes in living matter. Hydrogen bonding between two amide groups helps determine the protein structure, a topic that will be dealt with later, in Section 18-12.

18-6 Benzene and Its Derivatives

There is another important class of hydrocarbons, sometimes referred to as aromatic hydrocarbons. The simplest example is the compound benzene, a cyclic compound with the formula C_6H_6 and with six carbon atoms in a ring. The benzene ring is found to be planar with 120° angles between each pair of bonds formed by a given carbon atom. Experiment tells us the atoms of one molecule lie in a plane, with a regular arrangement.



We can easily decide how the carbon and hydrogen pairs are connected. The carbon-hydrogen distance is 1.08 Å, in good agreement with the carbon-hydrogen distance found for hydrocarbons. We can conclude that there is a single bond between each carbon and its neighboring hydrogen.

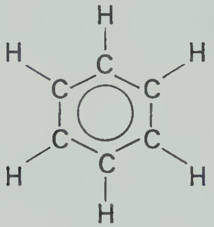


The carbon-carbon bonding gives more trouble. Some experimental data shows the problem. Some values of the carbon-carbon distance in various compounds are

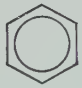
C—C	in ethane	1.54 Å	known single bond
C ? C	in benzene	1.40	
C═C	in ethylene	1.33	known double bond

The bond distances show that the benzene carbon-carbon bonds are intermediate to single and double bonds. The chemical behavior of the compounds in the list leads to the same conclusion. Benzene is more reactive than ethane. It reacts to a lesser degree, and in a different way, than ethylene does. In addition, all six carbon-carbon connections are found to be the same; in length and chemical behavior.

Several symbols have been used to show the intermediate character of the carbon-carbon bonding in benzene. We will use one that is consistent with current bonding theories. Benzene will be symbolized



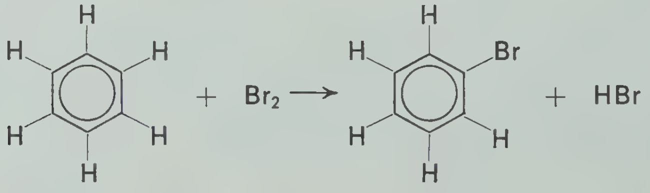
or



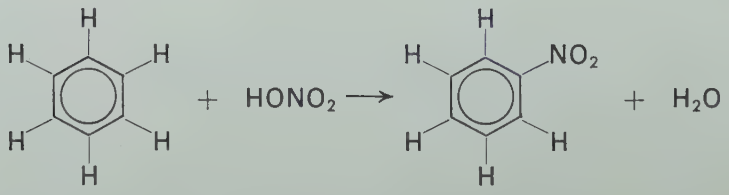
The straight line between carbon symbols *plus* the circle remind us that the bond is something more than a single C—C bond but different from a double C═C bond.

18-7 Benzene and Aromatic Compounds

Benzene is an unsaturated compound, but it does not behave in the same way that ethylene does. It does not *add* Br_2 but *substitutes* a bromine atom for one hydrogen.

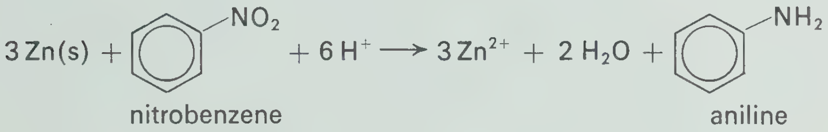


In this reaction, called bromination, one of the hydrogen atoms has been replaced by a bromine atom. Notice that the ring structure is not affected. This is not an addition reaction. Nitric acid causes a similar reaction, called nitration:

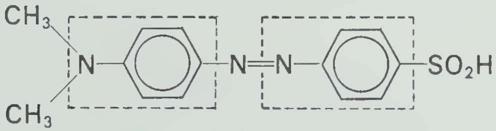


These reactions are called substitution reactions. The substitution reaction is the characteristic reaction of benzene and its derivatives and is the way in which a multitude of compounds are prepared by the organic chemist. Benzene and its derivatives are commonly called **aromatic compounds.**

Another important set of reactions involves modification of functional groups attached to the benzene ring. We will illustrate with nitrobenzene, one of the most important derivatives of benzene. The nitro group is —NO_2. Nitrobenzene is important chiefly because it can be readily reduced to an aromatic amine, aniline. One procedure uses zinc as the reducing agent.



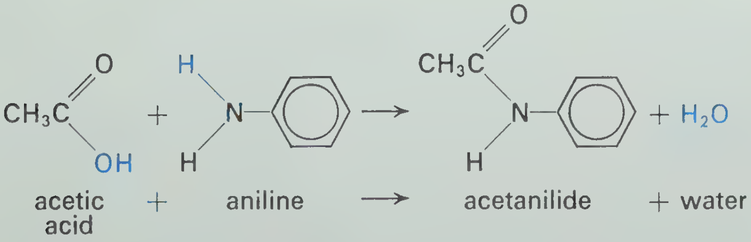
Aniline and other aromatic amines are valuable industrial raw materials. They serve as the starting point for the synthesis of many dyes and drugs. For example, you have used the indicator, methyl orange, in your laboratory experiments. Methyl orange is an example of a dye derived from aniline. The structure of methyl orange is as follows:



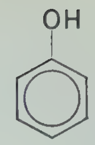
methyl orange

The portions of the methyl orange molecule set off by the broken lines come from aromatic amines like aniline. Aniline is indeed the starting material from which methyl orange and related dyes are made.

Another aniline derivative is acetanilide, which is the amide formed from aniline and acetic acid. Acetanilide is used medicinally as a pain-killing drug.

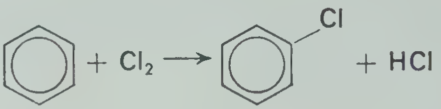


Another important compound that can be obtained from coal tar is hydroxybenzene, more commonly called phenol.

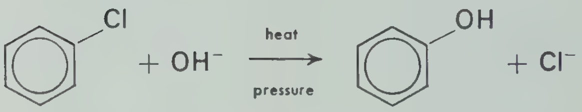


phenol

Most phenol is now made industrially from benzene, which is chlorinated as a first step. Reaction of chlorobenzene with base gives phenol:

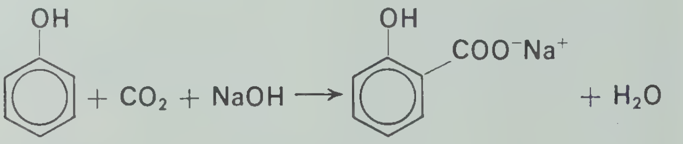


chlorobenzene

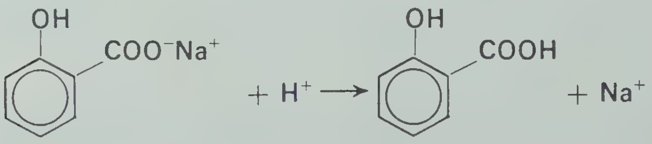


Phenol is a germicide and disinfectant. It was first used by Lister in 1867 as an antiseptic in medicine. More effective and less toxic antiseptics have since been discovered.

Perhaps the most widely known compound prepared from phenol is aspirin. If phenol, sodium hydroxide, and carbon dioxide are heated together under pressure, the sodium salt of salicylic acid is formed.

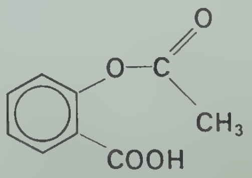


This salt reacts with acid to give salicylic acid.



salicylic acid

Salicylic acid is quite useful. Its methyl ester has a sharp, characteristic odor and is called "oil of wintergreen." The acid itself (or the sodium salt) is a valuable drug in the treatment of arthritis. But the most widely known derivative of salicylic acid is aspirin, which has the following structure:



aspirin

You will see, by examining this structure, that aspirin is an ester of acetic acid. Aspirin is mankind's most widely used drug. Somewhat over 20 million pounds of aspirin are manufactured each year in the United States alone! This amounts to something like 150 five-grain tablets for every person in the country! Figure 18-5 shows a portion of the process.

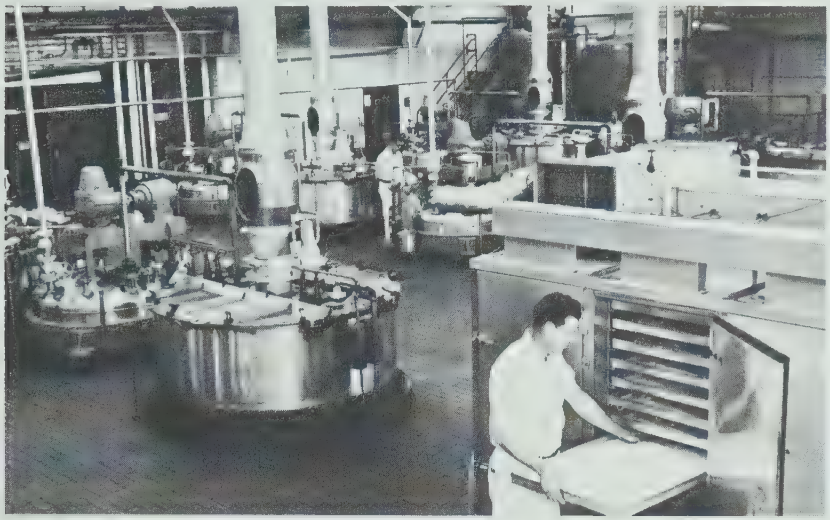


FIGURE 18-5

Part of a modern aspirin plant.

Benzene derivatives account for thousands of the known carbon-containing compounds. A few of them are listed in Table 18-1.

18-8 Polymers

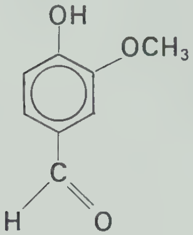
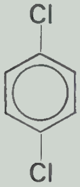
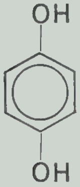
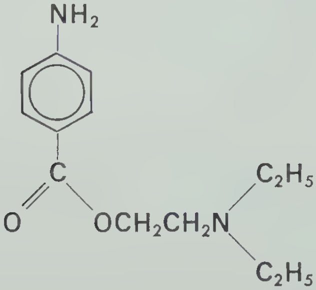
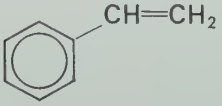
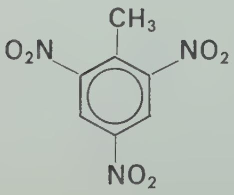
The melting temperatures of the normal alkanes tend to increase as the number of carbon atoms in the chain is increased. Ethane, C_2H_6, is a gas under normal conditions; octane, C_8H_{18}, is a liquid; octadecane, $C_{18}H_{38}$, is a solid. Desired physical properties can be obtained by controlling the length of the chain. Functional groups attached to the chain provide additional variability, including chemical reactivity. In fact, by adjusting the chain length and composition of compounds with high molar mass, chemists have produced a multitude of organic solid substances called plastics. These have been tailored for a wide variety of uses, giving rise to an enormous chemical industry.

The key to this chemical treasure chest is the process by which extended chains of atoms are formed. Inevitably it is necessary to begin with relatively small chemical molecules—with carbon chains involving only a few atoms. These small units, called **monomers,** must be bonded together, time after time, until the appropriate chain length is reached. Often the desired properties are obtained only with giant molecules, each containing hundreds or even thousands of monomers. These giant molecules are called **polymers** and the process by which they are formed is called **polymerization.**

Polymerization involves the chemical combination of many molecules to form a substance of high molar mass. Reactions that

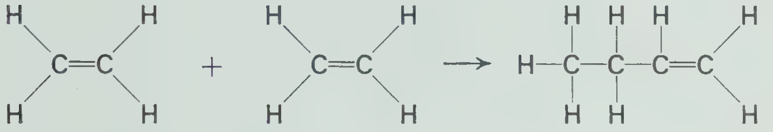
TABLE 18-1

Structures and Uses of Some Benzene Derivatives

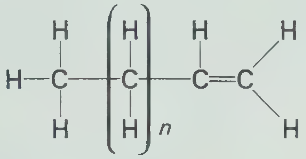
Structure	Name	Use
	vanillin	flavoring material
	*para*dichlorobenzene	mothballs
	hydroquinone	photographic developer
	Novocaine	local anaesthetic
	styrene	preparation of polystyrene plastics
	trinitrotoluene, TNT	explosive

combine many small molecules are referred to as addition polymerization or condensation polymerization.

Addition polymers are formed by the reaction of monomeric units without the elimination of atoms. The monomer is usually an unsaturated organic molecule such as ethylene, $H_2C{=}CH_2$. In the presence of a suitable catalyst, ethylene undergoes an addition reaction to form a long chain molecule, polyethylene. A general equation for the first stage of such a process can be written:

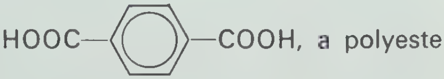


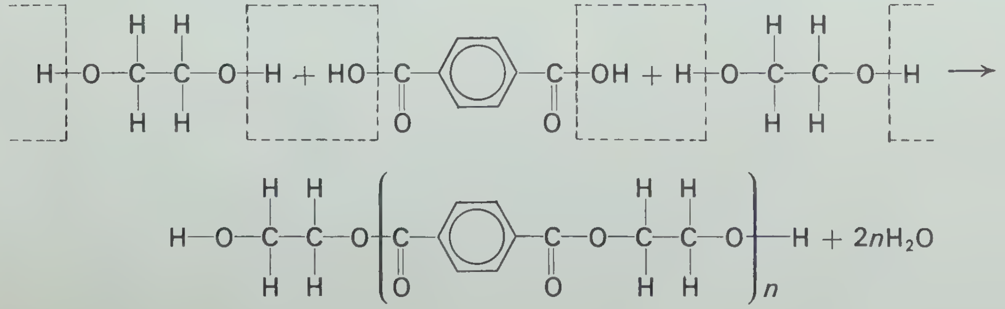
The same addition process continues and the final product is the polymer, polyethylene:



in which *n* is a very large number.

One or more of the hydrogen atoms in ethylene can be replaced by groups such as —F, —Cl, $—CH_3$, or $—COOCH_3$. The synthetic polymers with trade names such as Teflon, D Saran, Lucite, and Plexiglas result. It is possible to create molecules with custom-built properties for various uses as plastics or fibers.

The second major class of polymers, **condensation polymers,** is produced by reactions in which monomers join and a simple molecule such as water is eliminated. In order to form long chain molecules, two or more functional groups must be present in each of the reacting units. For example, when ethylene glycol, $HOCH_2CH_2OH$, reacts with *para*phthalic acid,  a polyester of high molar mass called Dacron is produced. The equation below shows the first stages of this process:



18-9 Nylon, a Polymeric Amide

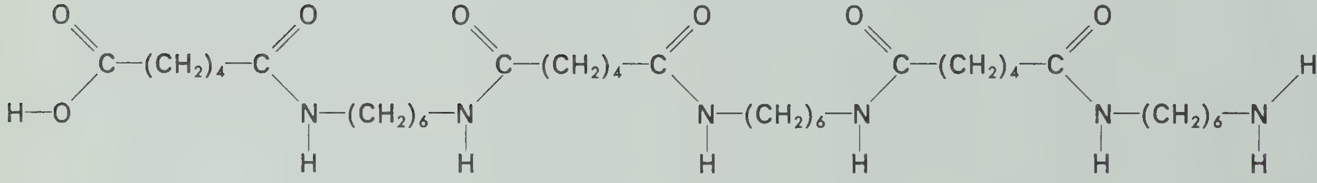
Nylon, the material widely used in plastics and fabrics, is a condensation polymer. It consists of molecules with extremely long chains. The reaction by which monomer units become bonded together is by amide formation between reactants with two functional groups. Polyamides can be made from one compound with two acid groups, adipic acid

$$\mathrm{HOOC{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}COOH}$$
$$\text{or } \mathrm{HOOC{-}(CH_2)_4{-}COOH}$$

and another with two amine groups, 1,6-diaminohexane

$$\mathrm{H_2N{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}NH_2}$$
$$\text{or } \mathrm{H_2N{-}(CH_2)_6{-}NH_2}$$

These molecules can react repeatedly, each time water is removed. Reaction of three amine and three acid molecules gives



A usable Nylon molecule would contain hundreds of these monomers. The linear structure of this molecule is the characteristic needed to produce a fiber.

BIOCHEMISTRY

Living organisms—bacteria, fungi, mosses, algae, plants, animals—are highly organized systems of chemical compounds. All organisms derive the energy for their activities, and produce the substances of which they are built, by means of chemical reactions.

A century and a half ago men regarded the chemistry of living organisms as something quite distinct from the chemistry of rocks, minerals, and other nonliving things. Indeed, there was in their minds at that time the inclination to believe that living things were imbued with some mysterious "vital force" that was beyond the power of men to define and understand.

As time went on, it became apparent that the mystery in the chemistry of living things was due to ignorance of the details of what went on. With an increased understanding of chemical principles, the mystery gradually began to disappear. Compounds that were earlier known only as the products of plants and animals were produced in the laboratory from inorganic substances. By the middle of the nineteenth century the superstitious belief in a chemical "vital force" had disappeared, and now there are few chemists who believe that the chemistry of living organisms is beyond the power of men to understand. We still, however, mark off a large area of chemical study by the term "biochemistry." Biochemists are chiefly concerned with the chemical processes that go on in living organisms. These scientists must use information from all branches of chemistry to answer the questions they ask. Their questions are usually something like, "What kind of molecules make up living systems?" or "How does a living system produce the energy it needs?"

Three classes of compounds that have great importance in biochemistry will be considered. Sugars are simple molecules which provide energy when they are oxidized. Cellulose and proteins are polymers that serve a double function, as foods and as structural elements in plants and animals.

18-10 Sugars, Simple Biological Compounds

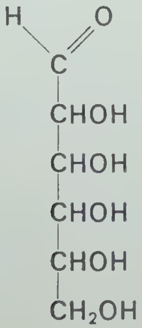
The word "sugar" brings to mind the sweet, white, crystalline grains found on any dinner table. The chemist calls this substance sucrose. It is one of many "sugars" which are classed together because they have related composition and similar chemical reactions. Sugars are part of the larger family of **carbohydrates**, a name given because many such compounds have the empirical formula CH_2O.

EXERCISE 18-7

Glucose, a sugar simpler than sucrose, has a molar mass of 180 g and empirical formula CH_2O. What is its molecular formula?

The structure of the glucose molecule was deduced by a series of steps somewhat like those described in Section 16-2 for ethanol. Glucose was found to contain one aldehyde group and five hydroxyl groups.

If all the oxygen containing groups are reduced, *n*-hexane results. This test helps establish that the glucose molecule has a chain structure. One representation of the structural formula of glucose, $C_6H_{12}O_6$, is

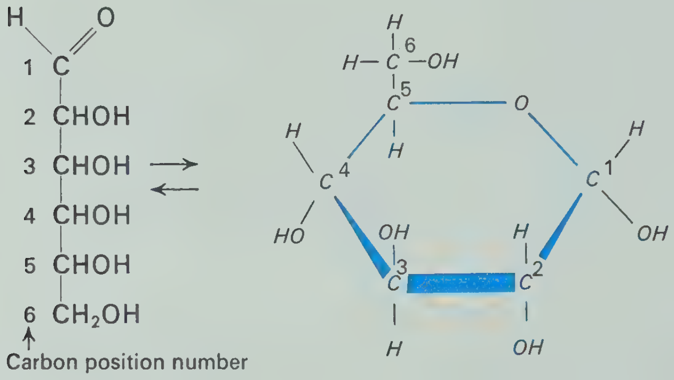


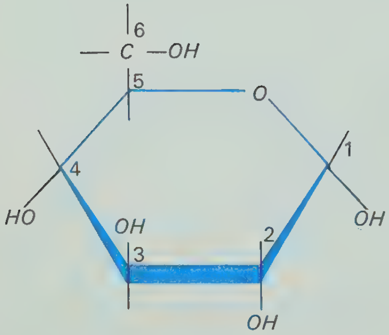
Another naturally occurring sugar is fructose, also $C_6H_{12}O_6$. It is an isomer of glucose. The carbon of the $>C{=}O$ group is at the second position in the carbon chain instead of at the end. It is a ketone.

EXERCISE 18-8

Draw a structural formula for the fructose molecule (remember that fructose is an isomer of glucose).

Glucose and fructose each exist as a straight chain molecule and as a cyclic structure. For each substance the two forms are in equilibrium. In solutions the latter form prevails. The equilibrium is shown for glucose.





The cyclic form can be written in a simpler way as at the left. The hydrogen atoms attached to carbon atoms are represented by lines only and the symbols for the carbons in the ring are omitted.

EXERCISE 18-9

At equilibrium in a 0.1 *M* solution of glucose in water, only 1% of the glucose is in the straight chain form. What is *K* for the reaction: chain $\rightleftarrows$ ring?

18-11 Disaccharides

The two sugars, glucose and fructose, are **monosaccharides.** They have a single sugar unit as the molecule. Table sugar is a disaccharide. It has two sugar units in the molecule. Sucrose contains one molecule of glucose and one of fructose joined together. Fructose has a slightly different ring structure because the $>C{=}O$ group is not on the end carbon. The structure of sucrose is shown in Figure 18-6.

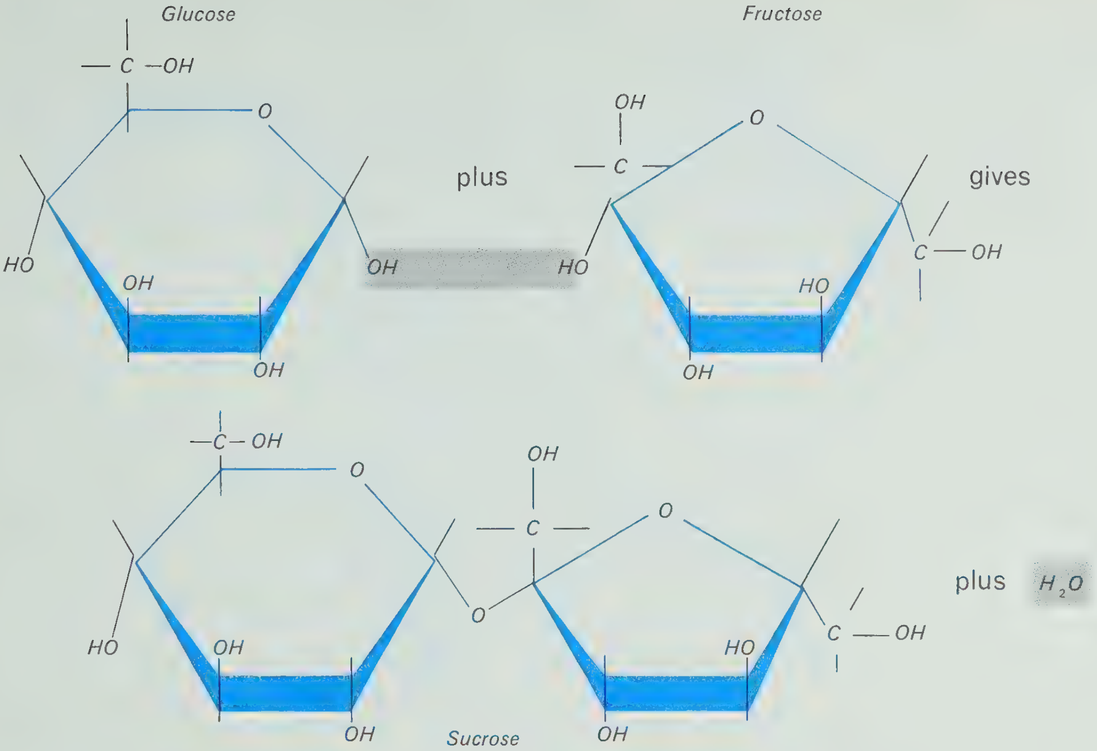
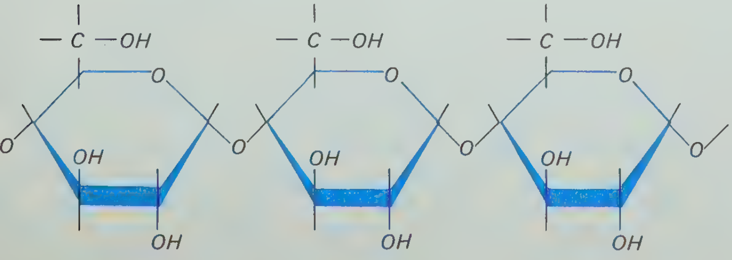


FIGURE 18-6 The condensation of two simple sugars to form the disaccharide, sucrose.

Sugars occur in many plants. Major commercial sources are sugar cane (a large, specialized grass which stores sucrose in the stem) and sugar beet (as much as 15% of the root is sucrose). In addition, fruits, some vegetables, and honey contain sugars. On the average every American eats almost 100 pounds of sugar per year. Sugar, at about 10 cents a pound retail, is one of the cheapest pure chemicals produced.

18-12 Some Biological Polymers: Starch, Cellulose, and Protein

Cellulose is an important part of woody plants, occurring in cell walls which make up part of the structural material of stems and trunks. Cotton and flax are almost pure cellulose. Chemically, cellulose is a polysaccharide. It is a polymer made by successive reactions



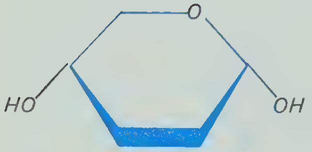
of glucose molecules to give a high molar mass, approximately 600,000 grams. This polymer is quite similar to the polymers that were discussed in Sections 18-8 and 18-9.

Starch is a mixture of glucose polymers, some of which are water-soluble. This soluble portion consists of comparatively short chains with molar mass near 4000 grams. The portion of low solubility involves much longer chains.

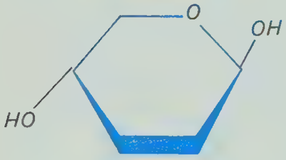
EXERCISE 18-10

The monomer unit in starch and that in cellulose each has the empirical formula $C_6H_{10}O_5$. These units are about 5.0 Å long. Approximately how many units occur and how long are the molecules of cellulose and of soluble starch?

A striking example of the effect of structure is shown by cellulose and water-soluble starch. Both contain the same monomer since hydrolysis gives only glucose in each case. But the glucose ring differs slightly in the arrangement of the OH groups. This results in two different polymers. The ring structure of glucose can be represented in an even more simplified form. Only the two hydroxyl groups that take part in polymerization are shown.



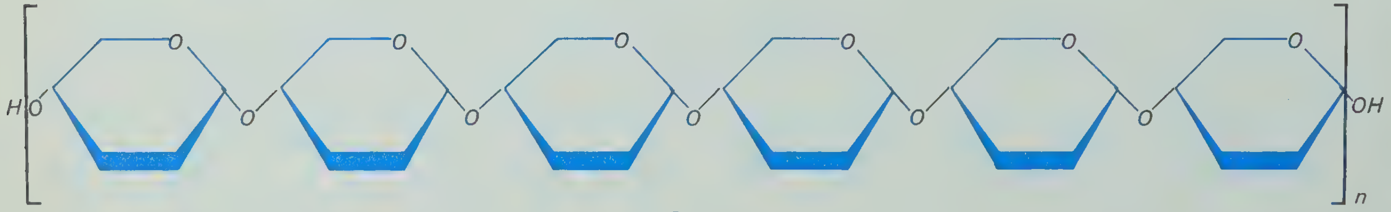
α-form



β-form

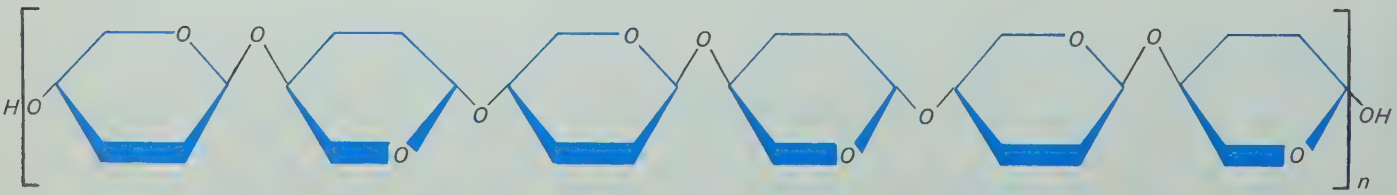
There is another isomer of glucose identical except for the geometry of the OH group on the right in the drawing.

Starch is the polymer formed when a large number of glucose molecules with the α-form react.



Starch

On the other hand, a chain of the β-form of glucose gives the polymer called cellulose:



Cellulose

The different geometry in starch and cellulose causes these two polymers to have different chemical properties.

A most important class of compounds is that of proteins, the essential structure of all living matter. Man needs protein in his diet as a source of amino acids. From these acids the body synthesizes different types of proteins, which are used to build various parts of the body.

Proteins are polyamides that are formed by the polymerization, through amide linkages, of α-amino acids. Three important α-amino acids are shown in Figure 18-7. Each acid has an amine group, —NH_2, attached to the α-carbon, the carbon atom immediately adjacent to the carboxylic acid group. The protein molecule may involve hundreds of such amino acid molecules connected through the amide linkages. A portion of this chain is represented as shown in Figure 18-8.

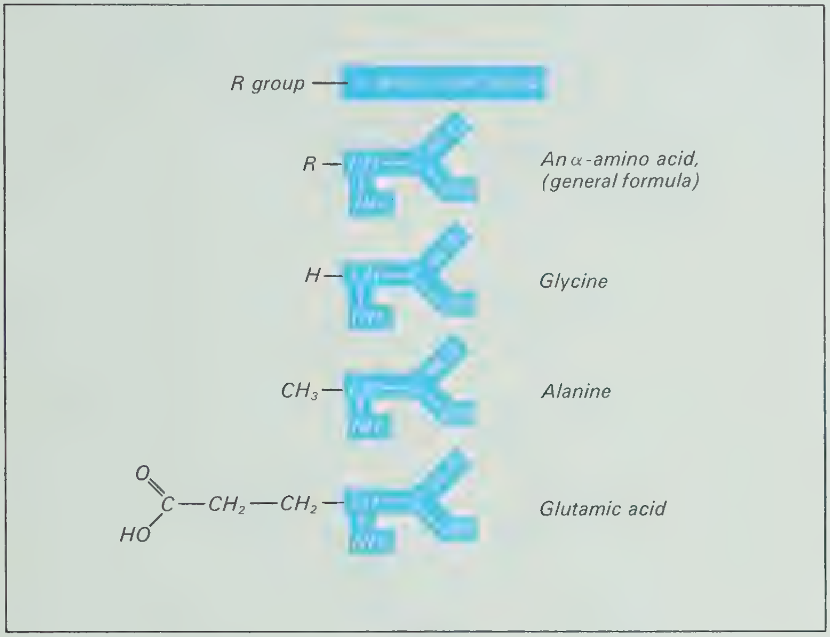

R group
R—
An α-amino acid,
(general formula)
H—
Glycine
CH3—
Alanine
O
C—CH2—CH2—
HO
Glutamic acid

FIGURE 18-7

Structures of some α-amino acids.

X-ray diffraction studies have led to the recognition of a coiled form of the chain in natural proteins. This form has a great deal

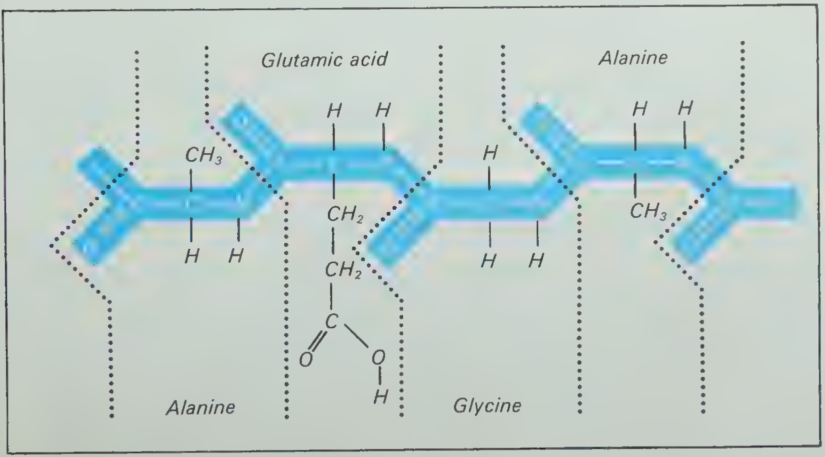

Glutamic acid
Alanine
H H
CH3
H
H H
CH2
CH2
C
O
O
H
H H
H H
CH3
Alanine
Glycine

FIGURE 18-8

A portion of an amide chain in a protein.

of regularity. It is not at all a random shape. Order is not achieved without some energy to maintain it, and this comes mainly from the formation of hydrogen bonds; those holding the white atoms in Figure 18-9. The hydrogen bonds can be broken by heating or by putting the protein in alcohol. The order disappears and the coiled form loses its shape. Often this damage cannot be repaired and the coil is permanently deformed. Cooking an egg destroys the coiled form of the proteins it contains. A few moments of thought concerning the profound differences between the physical form and between the chemical potentialities of an egg before and after it is cooked will suggest the very great importance of molecular structure in biochemistry.

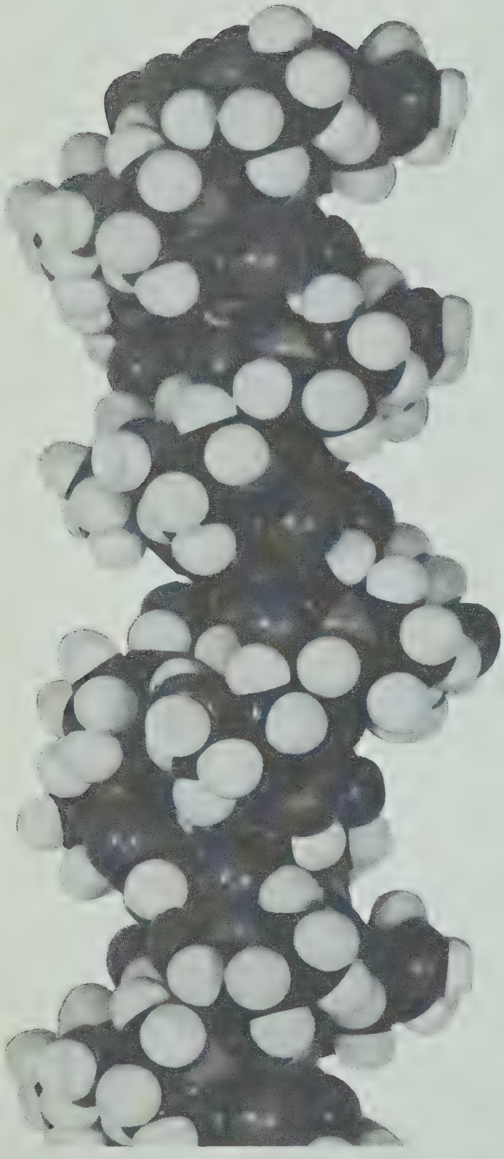


FIGURE 18-9

The coiled form of a protein.

18-13 Enzymes

Proteins act as catalysts for many of the reactions that take place in our bodies. The name *enzymes* has been given to these catalytic protein molecules. Usually enzyme molecules are very large, with a molar mass of about 100,000 grams being average. Compared with most chemicals that you have studied, these are enormous molecules. There are some important biochemical molecules that are considerably larger. The molar mass of hemoglobin in your red blood cells is about 500,000 grams, and some plant viruses have molar masses as high as 40,000,000 grams!

An enzyme molecule causes its catalytic action by forming weak bonds to a smaller molecule, called the substrate. In the form produced by this combination, the substrate molecule reacts faster than it would without the enzyme present. In 1966 the detailed structure of an enzyme, lysozyme, was determined for the first time. This enzyme increases the rate at which polysaccharides in bacterial walls are broken into smaller units.

Lysozyme is a chain of 129 amino acids. Portions of the polyamide chain are coiled as in Figure 18-9 while other portions are not coiled. The molecule as a whole has 1940 atoms and is about 40 Å wide in its largest dimension. Each lysozyme molecule has a shape somewhat like a cupped hand. A slot or valley in the molecule is the site that can hold the polysaccharide molecule. The shape of the valley and placement of the functional groups in it mean that only certain molecules can fit. These are the ones whose reactions are catalyzed by the enzyme. Again, molecular structure has a vital part in chemical behavior.

18-14 Energy Sources in Nature

Man and other animals use energy continuously, to maintain body temperature and for muscular activities such as breathing and moving around. The chief source of the needed energy is the oxidation of carbon compounds to CO_2. We can illustrate the process with sugar, one of the most important foods of animals. Man eats sugar either directly or as starch, the polymeric form in which sugar is stored in many plants, such as the potato. Cellulose, although a glucose polymer, is not useful to humans because our digestive systems cannot break the large molecules into glucose fast enough.

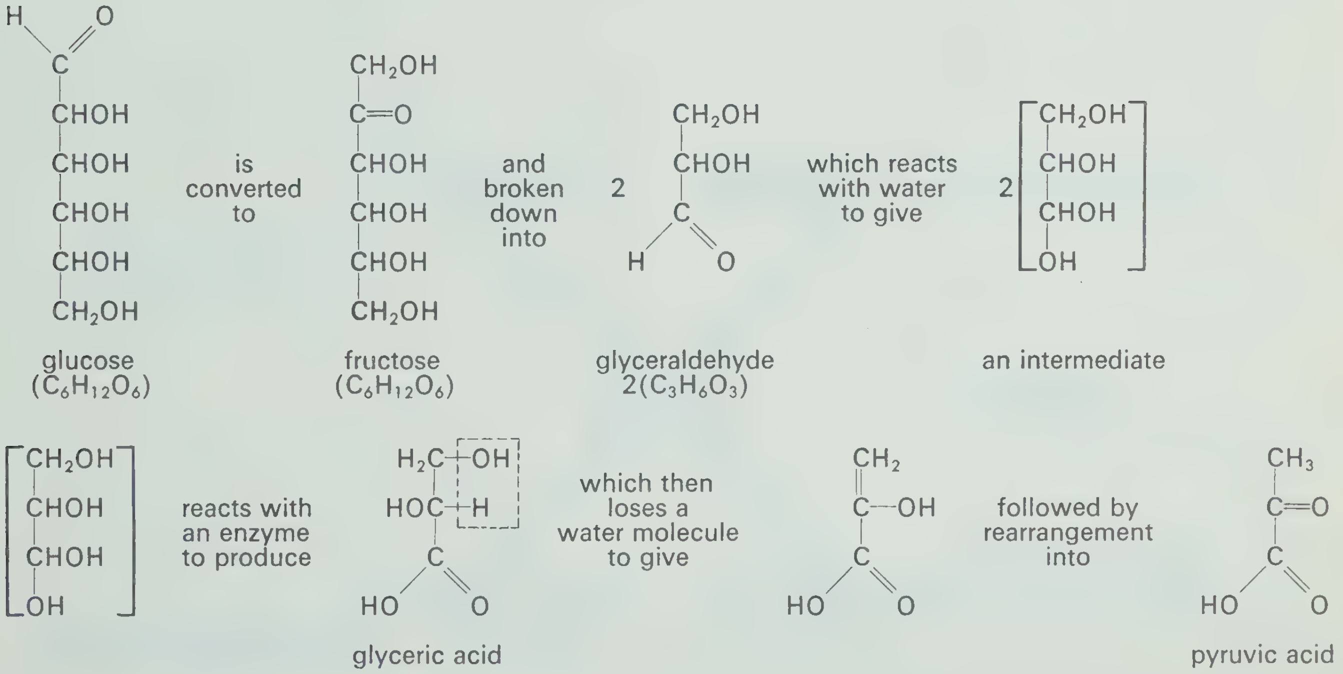
The process by which glucose is oxidized to yield CO_2, H_2O, and energy is very complex. We shall present only the major points and skip over numerous details. First, consider three major steps.

Glucose is converted to pyruvic acid.

Pyruvic acid is changed to acetic acid.

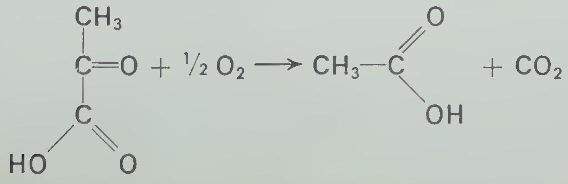
Acetic acid is oxidized to carbon dioxide, water, and energy.

We can picture the series of reactions in the following, much simplified manner.


is converted to
and broken down into
2
which reacts with water to give
2
glucose ($C_6H_{12}O_6$)
fructose ($C_6H_{12}O_6$)
glyceraldehyde 2($C_3H_6O_3$)
an intermediate
reacts with an enzyme to produce
which then loses a water molecule to give
followed by rearrangement into
glyceric acid
pyruvic acid

Throughout this stage there has been no oxidation, just addition and loss of water plus several rearrangements of the bonds. The energy needed by the human body does not come from these reactions.

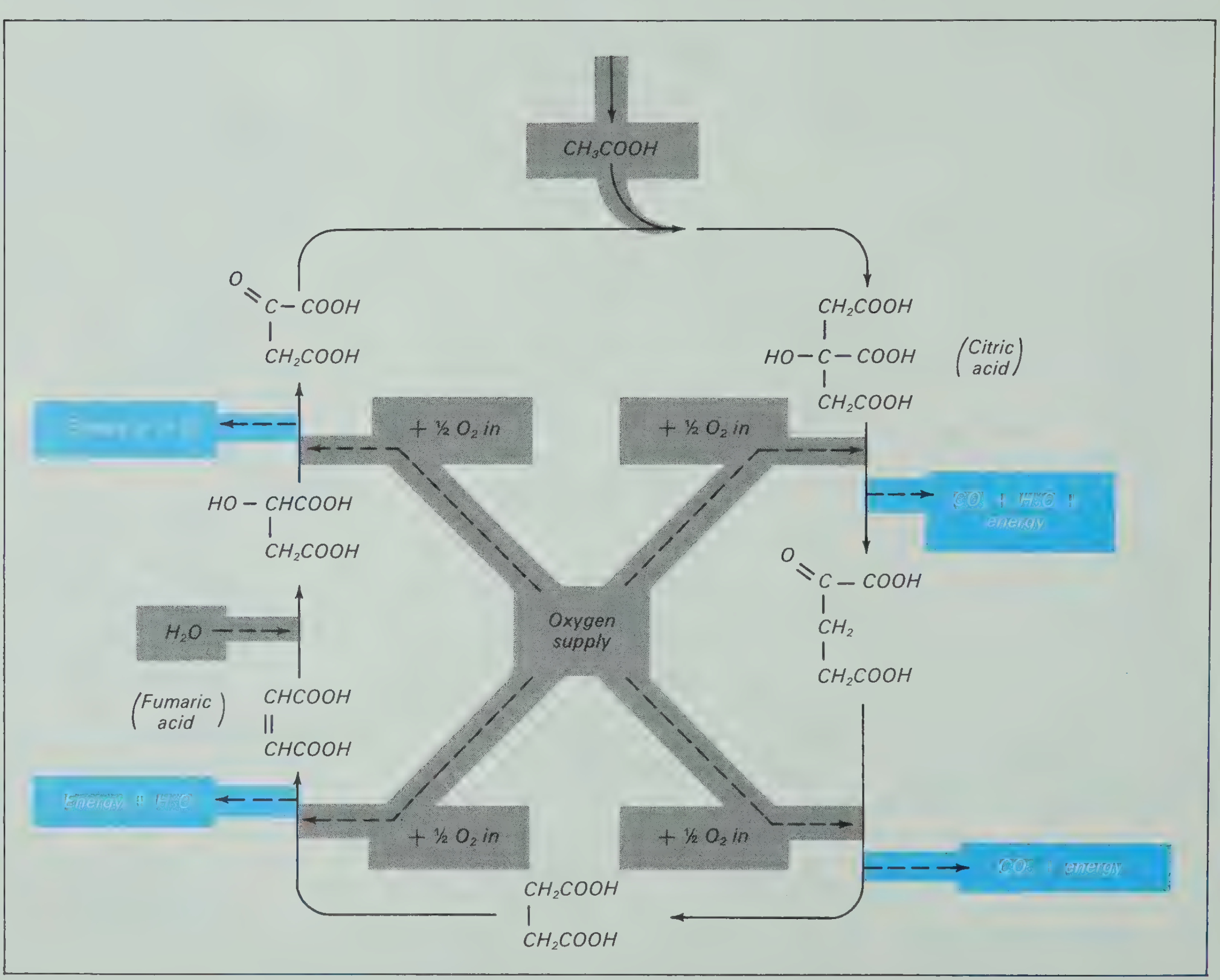
The second major step begins the use of oxygen.



$$CH_3COCOOH + \tfrac{1}{2}\,O_2 \longrightarrow CH_3COOH + CO_2$$

The acetic acid then enters a cycle of reactions to carry out the third major step. The cycle is shown in Figure 18-10. To oxidize each molecule of acetic acid this cycle uses two molecules of oxygen and produces two molecules of CO_2 and two of water. A great deal of energy comes from these reactions.

FIGURE 18-10 The cycle by which acetic acid provides energy.


CH_3COOH
CH_2COOH
$HO-C-COOH$
CH_2COOH
(Citric acid)
+ ½ O_2 in
CO_2 + H_2O + energy
$O=C-COOH$
CH_2
CH_2COOH
+ ½ O_2 in
CO_2 + energy
CH_2COOH
CH_2COOH
+ ½ O_2 in
Energy + H_2O
CHCOOH
||
CHCOOH
(Fumaric acid)
H_2O
$HO-CHCOOH$
CH_2COOH
Energy + H_2O
+ ½ O_2 in
$O=C-COOH$
CH_2COOH
Oxygen supply

Questions and Problems for Chapter 18

1

How much ethanol can be made from 50 grams of ethyl bromide? What assumptions do you make in answering this question?

2

Give the empirical formula, the molecular formula, and draw the structural formulas of the isomers of butene. This hydrocarbon contains four carbon atoms and one double bond.

3

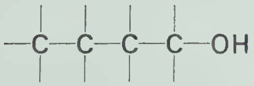
Ethane, C_2H_6, reacts with chlorine to substitute first one chlorine for hydrogen, then two, and so on until C_2Cl_6 is formed. How many different ethane derivatives form in this series of reactions?

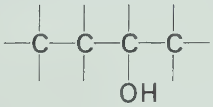
4

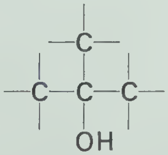
Write the balanced equation for the production of pentanone from pentanol, using dichromate ion as the oxidizing agent.

5

Knowing the possible oxidation products of ethanol and 2-propanol, predict the oxidation products of:







6

One mole of an organic compound is found to react with $^1/_2$ mole of oxygen to produce an acid. To what class of compounds does this starting material belong?

7

Using the information given in Table 11-2, determine the reaction heat per mole of $C_2H_6(g)$ for the complete combustion of ethane.

8

An aqueous solution containing 0.10 mole/liter of chloroacetic acid, ClH_2CCOOH, is tested with indicators and the concentration of $H^+(aq)$ is found to be 1.2×10^{-2} *M*. Calculate the value of K_A (if necessary, refer back to Section 14-8). Compare this value with K_A for acetic acid—the change is caused by the substitution of a halogen atom near a carboxylic acid group.

9

Give simple structural formulas of

(a) an alcohol,
(b) an aldehyde, and
(c) an acid,

each derived from methane; from ethane; from butane; from octane.

10

Write the equations for the preparation of methylamine from methyl iodide.

11

Show a two stage synthesis for the formation of butylamine starting with *n*-butyl alcohol, HI and NH_3.

12

Write equations using structural formulas and name the products for the reaction of acetic acid with

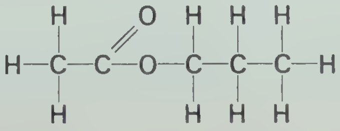
(a) ethyl alcohol
(b) ethylamine
(c) *iso*propylamine

13

Write equations to show the formation of the esters, methyl butyrate and butyl propionate.

14

Given the structural formula



for an ester, write the formula of the acid and the alcohol from which it might be made.

15

In the preparation of methyl acetate, the yield of ester is rather low at equilibrium. What can be done to increase the yield? Study the equation and apply Le Chatelier's Principle.

$$\begin{matrix}\text{methyl}\\\text{alcohol}\end{matrix} + \begin{matrix}\text{acetic}\\\text{acid}\end{matrix} \rightleftarrows \begin{matrix}\text{methyl}\\\text{acetate}\end{matrix} + \text{water}$$

16

How much acetamide can be made from 3.1 grams of methyl acetate? See equation on page 362. Assume the ester is completely converted.

Answer. 2.5 grams acetamide.

17

An ester is formed by the reaction between an acid, RCOOH, and an alcohol, R′OH, to form an ester RCOOR′ and water. The reaction is carried out in an inert solvent.

(a) Write the equilibrium relation among the concentrations, including the concentration of the product water.

(b) Calculate the equilibrium concentration of the ester if $K = 10$ and the concentrations *at equilibrium* of the other constituents are:

$[\text{RCOOH}] = 0.1\ M$;
$[\text{R'OH}] = 0.1\ M$;
$[H_2O] = 1.0\ M$.

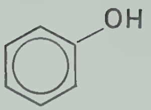
(c) Repeat the calculation of part *b* if the equilibrium concentrations are:

$[\text{RCOOH}] = 0.3\ M$;
$[\text{R'OH}] = 0.3\ M$;
$[H_2O] = 1.0\ M$.

18

There are three isomers of dichlorobenzene (empirical formula C_3H_2Cl). Draw the structural formulas of the isomers.

19

Consider the compound phenol, 

(a) Predict the angle formed by the nuclei C, O, H. Explain your choice in terms of the orbitals used by oxygen in its bonds.

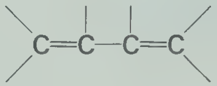
(b) Predict qualitatively the boiling temperature of phenol. (The boiling temperature of benzene is 80°C.) Explain your answer.

(c) Write an equation for the reaction of phenol as a proton donor in water.

(d) In a 1.0 M aqueous solution of phenol, $[H^+] = 1.1 \times 10^{-5}$. Calculate K_A.

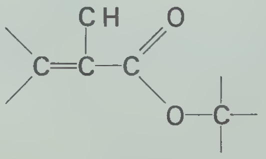
20

Work out a possible structural formula for the polymer of 1,3-butadiene,



21

Lucite is an addition polymer of methylmethacrylate, shown below



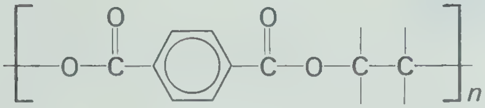
Draw a portion of the Lucite structure.

22

What types of bonds would you expect to bind the very long polyethylene molecules to each other? The long Nylon molecules to each other? Which polymer would you expect to melt at the lower temperature?

23

Dacron is a polyester made in a way similar to Nylon. The structure is



What alcohol is used in making Dacron?

24

Nylon and Dacron are made from monomers containing two functional groups per molecule. What type of polymers might result if a monomer had three or more functional groups?

25

Account for the fact that starch, a glucose polymer, is readily assimilated as food by humans but cellulose, also a glucose polymer, is not.

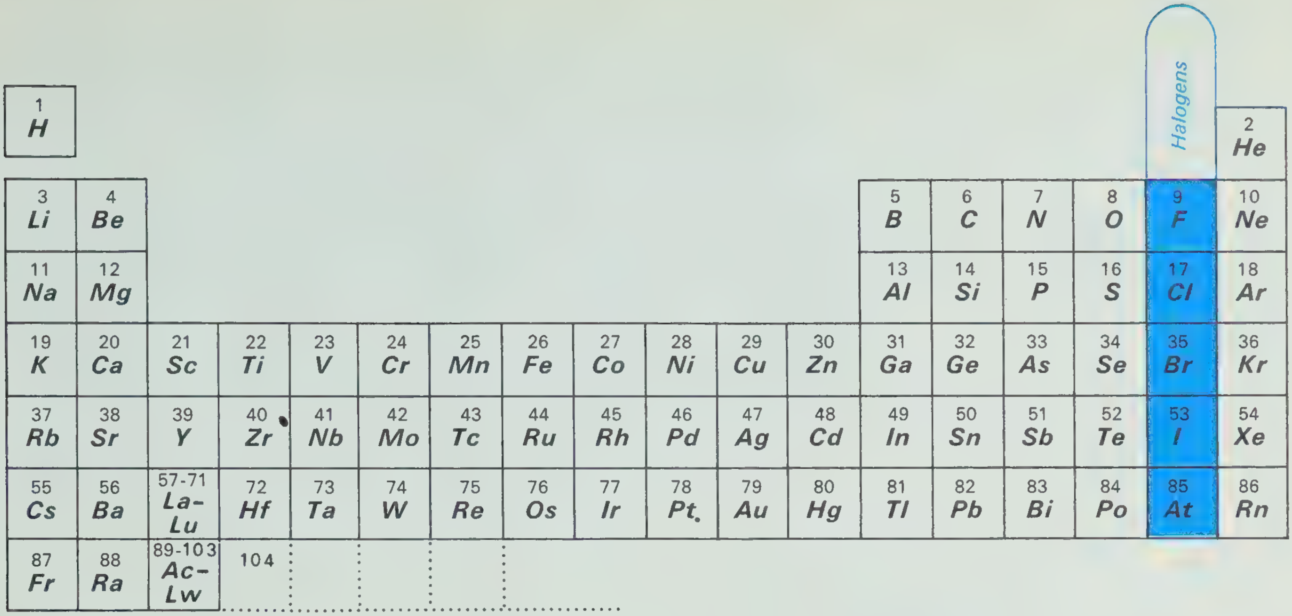
The Halogens

19

On many occasions in this book you have encountered the halogens and their compounds, both in your laboratory program and in class discussions. Some of the most important and most useful substances are derived from the elements fluorine, chlorine, bromine, and iodine. Element 85, astatine, is a member of the halogen family, but it is so rare that it will not be included in our discussion. Perhaps better than any other group of elements, the halogens show remarkable similarities and trends in chemical behavior.

In the nineteenth century chemists studied the halogens and wondered about these striking similarities. This family of elements provided many important clues to the periodic relations among the elements. Later, with an understanding of atomic structure, the long-sought explanation for periodic properties was obtained. Today it is easy for us to correlate a large body of experimental information with the electron populations of the elements. The trends within a family such as the halogens can be understood in terms of the increase in nuclear charge, number of electrons, and atomic size in going from fluorine to iodine. With all the information available today we sometimes forget that observations of chemical systems came first and that explanation came second.

The halogens are very reactive elements. Under normal conditions they exist as diatomic molecules in which the atoms are held together with covalent bonds. Fluorine and chlorine are gases at room temperature. Bromine is a liquid. Iodine is a solid with sufficient vapor pressure that a thin layer of crystals left out overnight will sublime away by morning. Halogen molecules absorb light in the visible region of the spectrum, and consequently the halogens are colored substances. Fluorine is light yellow, chlorine is yellowish-green, bromine is reddish-brown, and crystalline iodine is black (in the gas phase, iodine is purple). In their elementary state, the halogens are toxic and dangerous substances. Fluorine is the most hazardous. The danger *decreases* as the atomic number of the halogen *increases*. Nevertheless, even iodine, I_2, should be handled with care. However, the halogens form part of many compounds


Halogens
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
57-71 La-Lu
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
89-103 Ac-Lw
104

that are quite safe to handle. A fluorocarbon, dichlorodifluoromethane (CCl_2F_2), is used widely as a refrigerant and as the gas in aerosol cans.

19-1 Preparation and Properties of the Elements

The halogens are so reactive that they do not occur uncombined in nature. They must be made from halogen-containing compounds. Electrolytic oxidation is used to prepare fluorine and chlorine. Chlorine, for example, is made by electrolysis of molten sodium chloride. Figure 19-1 shows the components of the electrolysis cell. Molten sodium is produced at the cathode, and chlorine gas is collected at the anode.

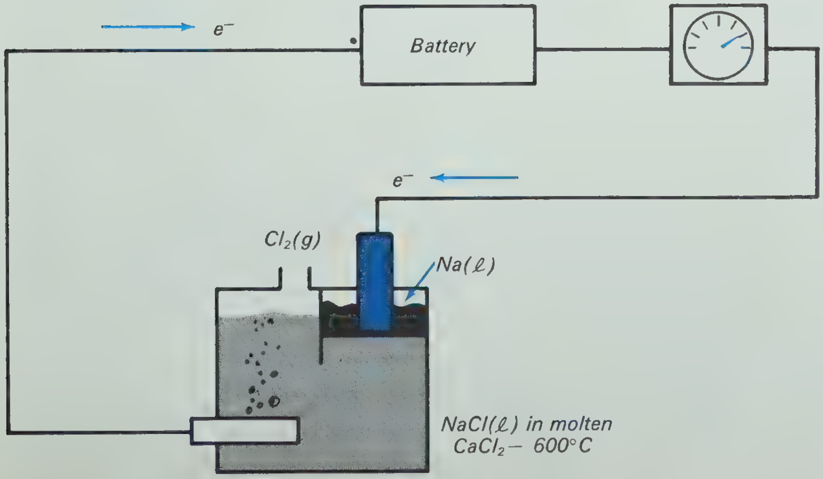

e^-
Battery
e^-
$Cl_2(g)$
$Na(\ell)$
$NaCl(\ell)$ in molten $CaCl_2$ — 600°C

FIGURE 19-1

Production of Cl_2 by electrolysis of molten NaCl.

Gaseous fluorine is prepared by electrolysis of molten KHF_2, using a copper vessel. Copper like most metals is attacked by fluorine. However, a layer of copper(II) fluoride forms, protecting the metal from rapid corrosion.

Chemical oxidation, usually with chlorine as the oxidizing agent, provides bromine and iodine economically because chlorine is a relatively inexpensive chemical. Most of the bromine in the United States comes from seawater, which contains about 0.005 weight percent of bromide ion. Iodine can be obtained from salt brines by oxidation of the iodides with chlorine.

The properties of the halogens are summarized in Table 19-1.

TABLE 19-1

Comparison of the Halogens

Property	F	Cl	Br	I
Melting temperature, °C	−223	−102	−7.3	113
Boiling temperature, °C	−188	−35	58	183
Color of gas	Light yellow	Yellowish-green	Reddish-brown	Purple
Valence electrons	$2s^22p^5$	$3s^23p^5$	$4s^24p^5$	$5s^25p^5$
Ionic radius of X^-, Å	1.36	1.81	1.95	2.16
van der Waals radius of X in X_2, Å	1.35	1.80	1.95	2.16
Covalent radius of X in X_2, Å	0.72	0.99	1.14	1.33
$E°$ in volts for $2\,X^- \longrightarrow X_2 + 2\,e^-$	−2.87	−1.36	−1.06	−0.53
Ionization energy for atom X, kcal/mole $X(g) \longrightarrow X^+(g) + e^-$	401.5	300	273	241
Ionization energy for ion X^-, kcal/mole $X^-(g) \longrightarrow X(g) + e^-$	81	86	80	73
Bond dissociation energy, kcal/mole $X_2(g) \longrightarrow 2\,X(g)$	37.8	58.0	46.2	36.1

The first four properties listed in Table 19-1 have been discussed several times in earlier sections of this book. The remaining properties illustrate trends within a family of elements. The significance of the three kinds of radii will be outlined first.

19-2 The Sizes of Halogen Atoms and Ions

The "size" assigned to an atom or ion requires a decision about where an atom "stops." According to the quantum mechanical model an atom has no sharp boundaries or surfaces. However, chemists find it convenient to assign sizes to atoms according to the observed distances between atoms. Atomic size is defined operationally. It is determined by measuring the distance between atoms.

For example, Figure 19-2 contrasts the dimensions assigned to the halogens in the elementary state. One-half the measured internuclear distance is called the **covalent radius.** This distance indicates how close a halogen atom approaches another atom to which it is bonded. To atoms with which it is not bonded, a halogen atom seems to be larger. One-half the average distance between neighboring molecules in the solid state defines the **van der Waals radius** shown by the blue lines in Figure 19-2. This radius indicates how closely nonbonded atoms approach.

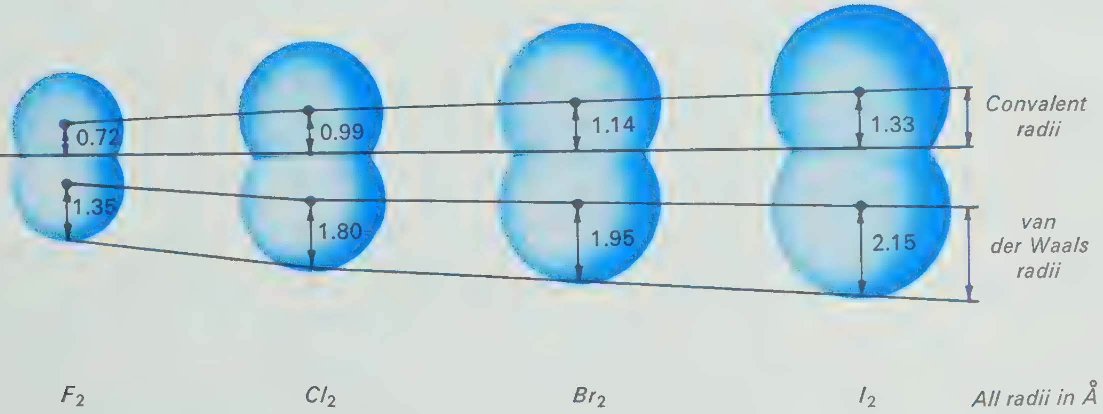


FIGURE 19-2 Covalent and van der Waals radii of the halogens.

Covalent radii aid in explaining and predicting bond lengths in other covalent halogen compounds. For example, when a chlorine atom is bonded to a carbon atom (as in carbon tetrachloride), it seems reasonable to expect the C—Cl bond length to be the sum of the covalent radii of the two elements, carbon and chlorine. From the diamond structure, the covalent radius for carbon is 0.77 Å. Combining this value with 0.99 Å, the covalent radius of chlorine, leads to a calculated C—Cl bond length of 1.76 Å. Experiment shows that each bond in CCl_4 is 1.77 Å.

EXERCISE 19-1

Use the carbon atom covalent radius 0.77 Å and the covalent radii given in Figure 19-2 to predict C—X bond length in each of the following molecules: CF_4, CBr_4, CI_4. Compare your values with the experimental ones:

C—F in CF_4 = 1.32 Å
C—Br in CBr_4 = 1.94 Å
C—I in CI_4 = 2.15 Å

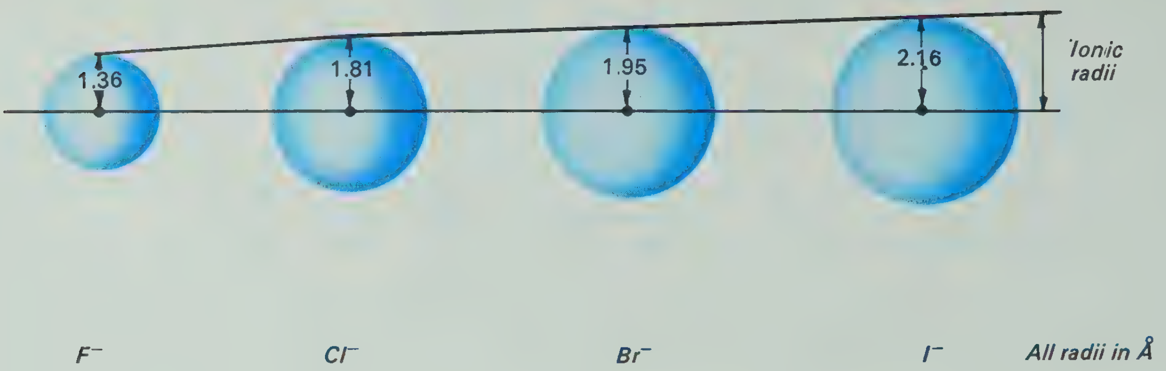


FIGURE 19-3

Ionic radii of the halogens.

Figure 19-3 contrasts the sizes of the halide ions. Each of these dimensions is obtained from the examination of crystal structures of many halide salts. The size found for a given halide ion is called its **ionic radius.** These radii are larger than the covalent radii but close to the van der Waals radii of neutral atoms.

The covalent, van der Waals, and ionic radii are presented in Table 19-1. We see some interesting trends. For each type of radius there is a gradual increase from fluorine to iodine. The increase in size reflects the fact that as atomic number rises, higher energy levels are used to accommodate the electrons. In addition, Table 19-1 shows a trend of increasing melting and boiling temperatures from fluorine to iodine. This trend is appropriate for a series of molecular solids in which van der Waals forces are the principal forces holding the molecules in their positions in the crystal.

19-3 The Oxidation-Reduction Properties of the Halogens

Most of the reactions of the halogens are oxidation-reduction reactions. The oxidizing abilities of the halogens vary in a regular manner, fluorine being the strongest and iodine the weakest. The equations and E° values for the half-reactions are:

$$\begin{aligned}
2\,I^- &\longrightarrow I_2 + 2\,e^- & E^\circ &= -0.53 \text{ volt}\\
2\,Br^- &\longrightarrow Br_2 + 2\,e^- & E^\circ &= -1.07 \text{ volts}\\
2\,Cl^- &\longrightarrow Cl_2 + 2\,e^- & E^\circ &= -1.36 \text{ volts}\\
2\,F^- &\longrightarrow F_2 + 2\,e^- & E^\circ &= -2.87 \text{ volts}
\end{aligned}$$

How can this trend in E° values and oxidizing powers be explained? It is often helpful to consider a series of simple, hypothetical steps whose sum is the equation for the half-reaction. For example:

$2\,I^-(aq) \longrightarrow 2\,I^-(g)$	Dehydration
$2\,I^-(g) \longrightarrow 2\,I(g) + 2\,e^-$	Electron removal from I^-
$2\,I(g) \longrightarrow I_2(g)$	Molecule formation
$I_2(g) \longrightarrow I_2(s)$	Condensation
$2\,I^-(aq) \longrightarrow I_2(s) + 2\,e^-$	Overall reaction

The energy requirements for these steps are presented in Table 19-2.

TABLE 19-2

ΔH Values for Some Halogen Reactions at 25°C

	ΔH, kcal/mole			
Reaction	F	Cl	Br	I
Dehydration $2\,X^-(aq) \longrightarrow 2\,X^-(g)$	246	178	162	144
Electron removal from X^- $2\,X^-(g) \longrightarrow 2\,X(g) + 2\,e^-$	162	171	161	146
Molecule formation $2\,X(g) \longrightarrow X_2(g)$	−37	−58	−46	−36
Condensation $X_2(g) \longrightarrow X_2(\text{normal state})$	−1.6 (g)	−4.4 (g)	−7 (*l*)	−10 (s)
Overall reaction $2\,X^-(aq) \longrightarrow X_2 + 2\,e^-$	369	287	270	244

Compare the ΔH values derived above with the $E°$ data given below.

$E°$, volts, overall reaction	−2.87	−1.36	−1.07	−0.53

The energy effects for the overall reactions can be discussed in terms of the energy effects in the various steps. The large positive values for ΔH indicate that the reactions are endothermic. The trend in ΔH values for the overall reaction is roughly comparable to the trend in $E°$ values. The half-reaction having the most negative $E°$ is the one that requires the most energy and shows the greatest tendency to favor reactants at equilibrium.

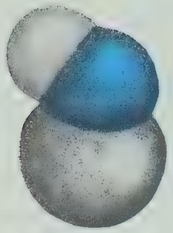
Notice that in Table 19-2 dehydration and electron removal of the ions are the steps that require the largest energy changes. For fluorine, dehydration is the major factor determining the overall energy of the half-reaction. The small ionic radius for fluoride ion suggests that there would be strong interaction between the negative ions and the electric dipole of the solvent, water. This explains why F_2 is a much stronger oxidizing agent than the other halogens.

The halogens are reactive even without water and react quite vigorously with most of the metals to produce simple halide salts. Here are a few examples:

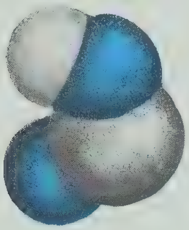
$$2\,Na + Br_2 \longrightarrow 2\,NaBr$$

$$Mg + F_2 \longrightarrow MgF_2$$

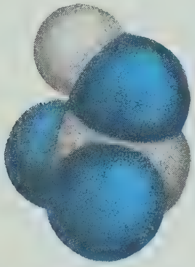
$$2\,Fe + 3\,Cl_2 \longrightarrow 2\,FeCl_3$$



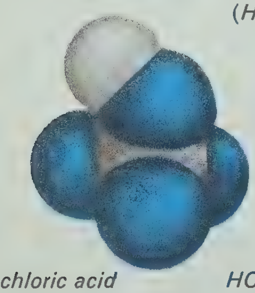
Hypochlorous acid *HOCl*



Chlorous acid *HOClO* $(HClO_2)$



Chloric acid *HOClO*$_2$ $(HClO_3)$



Perchloric acid *HOClO*$_3$ $(HClO_4)$

FIGURE 19-4

Presumed structures of the chlorine oxyacids.

19-4 Positive Oxidation States of the Halogens: The Oxyacids

With the exception of fluorine, the halogens can be oxidized to positive oxidation states. Most frequently, positive oxidation states are encountered in a set of compounds called "halogen oxyacids" and their ions.

Compounds of the type $HClO_3$ and $HClO_4$ are examples of the oxyacids. Chlorine forms a series of acids in which the halogen oxidation number can be +1, +3, +5, or +7. For chlorine the series is:

$HClO$	Hypochlorous acid
$HClO_2$	Chlorous acid
$HClO_3$	Chloric acid
$HClO_4$	Perchloric acid

Aqueous solutions of the acids have been studied to find out how strong they are as proton donors. One finds a regular trend: $HClO$ is a weak proton donor, $HClO_2$ is somewhat stronger, $HClO_3$ is quite strong, and $HClO_4$ is the strongest in this series. Perchloric acid, $HClO_4$, is one of the strongest acids known.

Can the observed trend in acid strength be accounted for in terms of structure and bonding in the oxyacids? Figure 19-4 shows the positions of the atoms in these molecules. It is evident that in each case a hydrogen-oxygen bond must be broken in order to split off the proton. A regular decrease in the strength of the hydrogen-oxygen bond from chlorous to perchloric acid would explain the trend in acidity. Can a variation in the strength of this bond be explained? The oxidation number of chlorine is changing from +1 to +3 to +5 to +7 in these compounds. More to the point there is an increasing number of oxygen atoms bonded to the central chlorine. Each time an additional oxygen bonds to the chlorine atom, some electric charge is drawn off the chlorine and away from the original O—Cl bond. This in turn draws electrons from the adjacent H—O bond and thereby weakens it.

This increase in acid strength with oxidation number is a general phenomenon. For example, in nitric acid, HNO_3, nitrogen has the oxidation number +5. Nitric acid is a stronger acid than nitrous acid, HNO_2, with oxidation number +3 for nitrogen. Sulfuric acid, H_2SO_4, with oxidation number +6 for sulfur, is a stronger acid than sulfurous acid, H_2SO_3, where sulfur has the oxidation number +4. A useful explanation is found. When an oxygen atom is added to the central atom, O—H bonds in the molecule are weakened.

19-5 The Importance of the Halogens and Their Compounds

There are many ways in which the halogens and their compounds are important. Table 19-3 summarizes a few examples.

TABLE 19-3

Major Uses for the Halogens

Halogen	Used to Prepare
Fluorine	Plastics such as Teflon. Catalysts in some petroleum processes. SnF_2 for fluoride toothpastes. NaF, an insecticide.
Chlorine	Br_2 and I_2. HCl, an important acid. $CaOCl_2$ for bleaching and disinfecting. Chlorates and perchlorates for matches, fireworks, explosives.
Bromine	$C_2H_4Br_2$, an important gasoline additive (to remove Pb produced from tetraethyl lead). AgBr for photographic emulsions.
Iodine	Disinfectants. Dyes and other organic compounds. AgI for photographic emulsions. Iodized salt, to prevent and cure goiter and other thyroid disorders.

19-6 Photography

One of the major uses of the halogens, particularly bromine, is in photographic emulsions. The silver salts of the halogens are light-sensitive. They decompose to form metallic silver and the free halogen when exposed to light. Black-and-white photography is based on this property of the silver halides. A photographic film is a sheet of transparent plastic covered with a thin layer of gelatin. Very fine crystals of AgBr are suspended in the gelatin. The process of changing unexposed film into a finished print can be outlined in four steps.

Exposure. When the film is exposed by opening the camera shutter, an image is produced in the film by light reflected from the object being photographed. The whiter the object, the larger is the amount of reflected light. Crystals of AgBr, in the areas where light strikes the film, are sensitized by some process not yet well understood. Sometimes the words "latent" or "hidden" image are used to describe the film at this stage. In a darkroom, using red light that does not affect the film, this image is not visible.

Development. The film is developed by placing it in a solution that contains a weak reducing agent such as hydroquinone. The sensitized AgBr crystals react at a much faster rate than do AgBr crystals not struck by light. The rate of this reaction is related to the intensity of light striking a crystal. The chemical reaction that takes place can be represented as

$$AgBr + \text{reducing agent} \longrightarrow Ag + Br^- + \text{oxidized products from the reducing agent}$$

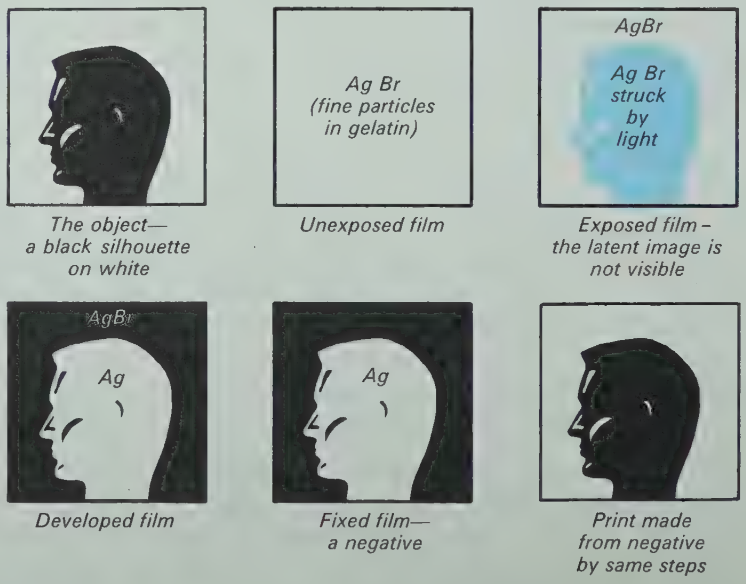
Metallic silver forms in the emulsion. Development of the latent image is carefully timed to produce black, white, and grey regions that have the desired relative intensities. The white areas of the object photographed show up as dark regions of silver in the film. When the developing process reaches the proper stage, the film is removed from the developing solution and put into a "stop bath" to destroy the unused reducing agent. It is then washed, and placed in the "fixing" solution.

Fixation. Some AgBr crystals have been reduced to metallic silver. The remaining AgBr crystals must now be removed from the emulsion. Otherwise the entire negative will turn black when exposed to light. This is done by reaction with sodium thiosulfate, often called "hypo."

$$AgBr + 2\,S_2O_3^{2-} \longrightarrow Ag(S_2O_3)_2^{3-} + Br^-$$

The film is thoroughly washed with water and then allowed to dry. At this stage, the film is called the *negative*. The white areas of the object have been recorded in the emulsion as black metallic silver regions; the dark areas of the object appear as transparent regions in the emulsion because AgBr has been removed.

Printing. A positive print is made by passing light through the negative onto a piece of print paper. This paper contains a layer of AgBr crystals, too. After exposing, developing, and fixing this print, one has a *positive* which duplicates the light and dark portions of the original object. Figure 19-5 shows schematically what takes place.



The object— a black silhouette on white

Unexposed film

Exposed film – the latent image is not visible

Developed film

Fixed film— a negative

Print made from negative by same steps

FIGURE 19-5

The steps in making a photograph.

19-7 Special Remarks on Fluorine

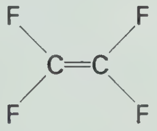
Because of the small size of the atom, fluorine is rather special in the halogen group. It is a very strong oxidizing agent in aqueous solution. One special property of fluorine is revealed when the properties of hydrogen fluoride are compared with the other hydrogen halides. See Figure 10-6, page 186. These properties can be explained in terms of the strong hydrogen bonding which occurs because of the small size of fluorine. Also, in aqueous solution hydrogen fluoride, HF, is a weak acid, whereas HCl, HBr, and HI are strong acids. The equilibrium constant for HF is 6.7×10^{-4}; so hydrofluoric acid is less than 10% ionized in a 0.1 *M* HF solution.

Another unusual property of HF is its reactivity with glass. Hydrofluoric acid cannot be kept in glass bottles because it reacts with the silica, SiO_2, in glass. On the other hand, even the most concentrated hydrochloric acid solutions can remain indefinitely in glass without any evidence of a comparable reaction. Polyethylene or wax containers are often used to store HF solutions. Silicon bonds more strongly to fluorine than to oxygen, and therefore silica dissolves in a solution of HF. The equation is

$$SiO_2 + 6\,HF \longrightarrow SiF_6^{2-} + 2\,H_3O^+$$

In many cities in the United States, a very small amount of fluoride ion, F^-, is added to the drinking water supply. The presence of fluoride ion has been shown to reduce tooth decay in children.

The carbon-fluorine bond is a very stable bond. The strength of the C—F bond is comparable to the strength of the C—H bond. This fact has led chemists to synthesize a series of compounds known as *fluorocarbons.* These are analogous to the hydrocarbons and can be imagined as derived from them by substituting F atoms for H atoms. For example,



is the fluorocarbon analogue of ethylene.

Polymeric fluorocarbons, such as Teflon, are being used in many new ways each year. They find extensive use in gaskets, valves, stopcocks, and fittings for handling corrosive chemicals. Teflon-coated cooking pans have become popular because foods do not stick to these pans. In the "protective coating," fluorine atoms are bonded so strongly to the carbon chain of these polymer coatings that they show almost no tendency to react with other substances.

Questions and Problems for Chapter 19

1

Give the electron configuration for each of the trio F^-, Ne, Na^+. How do the trios Cl^-, Ar, K^+, and Br^-, Kr, Rb^+ differ from the above?

2

Table 19-1 contains values for the covalent radii and the ionic radii of the halogens. Plot both radii versus row number. What systematic changes are evident in the two curves?

3

Using the data from Table 19-1, plot on one set of axes the melting and boiling temperatures of the halogens versus row number.

4

For astatine, use your graphs from Problems 2 and 3 as a basis for a prediction of its covalent radius, ionic radius of the At^- ion, melting and boiling temperatures.

5

Predict the molecular structures and bond lengths for SiF_4, $SiCl_4$, $SiBr_4$, and SiI_4, assuming the covalent radius of silicon is 1.16 Å.

6

Explain in terms of nuclear charge why the K^+ ion is smaller than the Cl^- ion, though they are isoelectronic (they have the same number of electrons).

7

Can aqueous bromine, Br_2, be used to oxidize ferrous ion, Fe^{2+}, to ferric ion, Fe^{3+} (use Appendix 4)? Can aqueous iodine, I_2, be used instead of bromine?

8

What will happen if F_2 is bubbled into 1 *M* NaBr solution? Justify your answer using $E°$ values.

9

Use $E°$ values to predict what will happen if chlorine is added to a 1 *M* solution of Br^-, of I^-. What will happen if Br_2 is added to 1 *M* I^-? Which halogen is oxidized and which is reduced in each case?

10

Write a balanced equation for the reaction of dichromate and iodide ions in acid solution. Determine $E°$ for the reaction

$$Cr_2O_7^{2-} + I^- + H^+ \text{ gives } Cr^{3+} + I_2 + H_2O$$

Answer. $E° = +0.80$ volt.

11

Balance the equation for the reaction of iodine with thiosulfate ion:

$$I_2 + \underset{\substack{\text{thiosulfate}\\\text{ion}}}{S_2O_3^{2-}} \text{ gives } \underset{\substack{\text{tetrathionate}\\\text{ion}}}{S_4O_6^{2-}} + I^-$$

What is the oxidation number of sulfur in the tetrathionate ion?

12

How many grams of iodine can be formed from 20.0 grams of KI by oxidizing it with ferric chloride ($FeCl_3$)? Determine $E°$.

Answer. 15.3 grams of I_2.

13

Balance the equation for the reaction between SO_2 and I_2 to produce SO_4^{2-} and I^- in acid solution. Calculate $E°$. From Le Chatelier's Principle, predict the effect on the $E°$ in this reaction if $H^+ = 10^{-7}$ *M* is used instead of $H^+ = 1$ *M*.

14

What is the oxidation number of the halogen in each of the following: HF, $HClO_2$, HIO_3, BrO_3^-, F_2, ClO_4^-?

15

Comparable half-reactions for iodine and chlorine are shown below.

$$\tfrac{1}{2}\,I_2 + 3\,H_2O \longrightarrow IO_3^- + 6\,H^+ + 5\,e^- \qquad E^\circ = -1.195 \text{ volts}$$

$$\tfrac{1}{2}\,Cl_2 + 3\,H_2O \longrightarrow ClO_3^- + 6\,H^+ + 5\,e^- \qquad E^\circ = -1.47 \text{ volts}$$

(a) Which is the stronger oxidizing agent, iodate, IO_3^-, or chlorate, ClO_3^-?
(b) Balance the equation for the reaction between chlorate ion and I^- to produce I_2 and Cl_2.

16

Two half-reactions involving chlorine are

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \qquad E^\circ = -1.36 \text{ volts}$$

$$Cl_2 + 2\,H_2O \longrightarrow 2\,HOCl + 2\,H^+ + 2\,e^- \qquad E^\circ = -1.63 \text{ volts}$$

(a) Balance the reaction in which self-oxidation-reduction of Cl_2 occurs to produce chloride ion and hypochlorous acid, HOCl.
(b) What is the oxidation number of chlorine in each species containing chlorine?
(c) What is E° for the reaction?
(d) Explain, using Le Chatelier's Principle, why the self-oxidation-reduction reaction occurs in 1 M OH^- solution instead of 1 M H^+.

17

From each of the following sets, select the substance which best fits the requirement specified.

(a) Strongest acid	HOCl, HOClO, $HOClO_2$
(b) Biggest atom	F, Cl, Br, I
(c) Smallest ionization energy	F, Cl, Br, I
(d) Best reducing agent	F^-, Cl^-, Br^-, I^-
(e) Weakest acid	HF, HCl, HBr, HI
(f) Strongest hydrogen bonding	HF, HCl, HBr, HI

18

Describe two properties that the halogens have in common and give an explanation of why they have these properties in common.

19

How many grams of SiO_2 would react with 5.00×10^2 ml of 1.00 M HF to produce SiF_4?

20

A water solution that contains 0.10 M HF is 8% dissociated. What is the value of K_A?

Answer. 6.9×10^{-4}.

The Fourth-Row Transition Elements

20

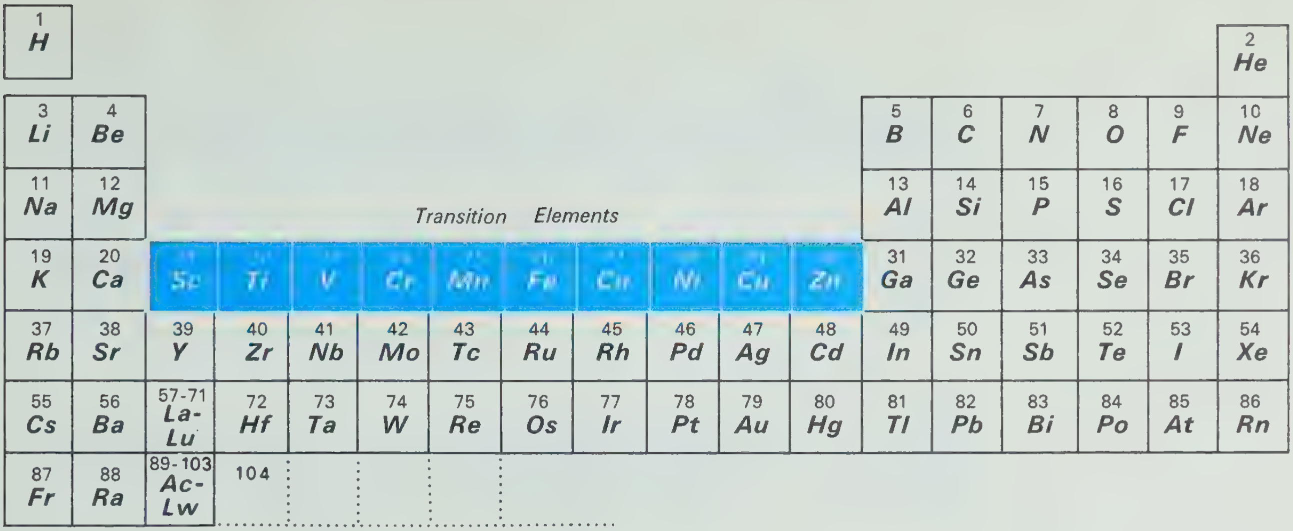
In preceding chapters the chemical properties of many of the elements across the top of the Periodic Table and down the two sides have been presented. Now some of the elements in the middle section will be considered. These elements are often referred to as the *transition elements.* Chemists once believed that these elements behaved in a fashion intermediate between the extremes shown by the chemical families on the left and right sides of the Periodic Table. Today the term "transition element" is still a useful way to designate elements in the middle of the Periodic Table.

When the elements in families such as the alkali metals or the halogens are compared, the similarities in chemical properties are very striking. The electronic designations and the ionization energies for these elements help explain this behavior. On the other hand, when the elements sodium through chlorine are compared, the contrasts in chemical properties are equally striking. The trends in acid-base and redox properties can be explained in terms of the great differences in electronic structure and ionization energy as we move horizontally across a row in the Periodic Table.

In this chapter the first group of transition elements, scandium through zinc, will be examined. In Chapter 9, when the electron configurations for the elements were being discussed, it was pointed out that the regular pattern of filling *s* and *p* orbitals was interrupted when the 21st element, scandium, was reached. The electron configuration for calcium is shown in Figure 20-1. Let us examine the electron configurations for Sc and the next nine elements.

20-1 Electron Configurations

The element scandium contains one more electron than calcium. The 21st electron enters the lowest energy orbital that is not fully


1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
Transition Elements
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
57-71 La-Lu
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
89-103 Ac-Lw
104

occupied. Figure 20-1 shows that this is a 3*d* orbital. There are five 3*d* orbitals. Putting a pair of electrons in each of these orbitals means that ten electrons can be accommodated before the higher energy 4*p* orbitals are needed. The fourth-row transition elements have the electron configurations shown in Table 20-1. In discussing valence electrons for the transition elements chemists include *d* electrons whereas *s* and *p* electrons were the only ones needed for nontransition elements.

TABLE 20-1

The Electron Configurations of the Fourth-Row Transition Elements

				Electron Configuration beyond an Argon Core	
Element	Symbol	Atomic number, Z	Argon core	3*d*	4*s*
Scandium	Sc	21	$1s^2$ $2s^22p^6$ $3s^23p^6$	1	2
Titanium	Ti	22		2	2
Vanadium	V	23	Each	3	2
Chromium	Cr	24	fourth-row	5	1
Manganese	Mn	25	transition	5	2
Iron	Fe	26	element	6	2
Cobalt	Co	27	has these	7	2
Nickel	Ni	28	orbitals	8	2
Copper	Cu	29	filled.	10	1
Zinc	Zn	30		10	2

Notice that chromium (Z = 24) and copper (Z = 29) provide interruptions to the regular buildup. In chromium, the gas-phase atom has lower energy if one of the 4*s* electrons moves into the 3*d* set. This gives chromium a half-filled set of 3*d* orbitals and a half-filled 4*s* orbital. In copper, the atom has lower energy if the 3*d* set is completely filled with ten electrons and the 4*s* orbital is half-filled.

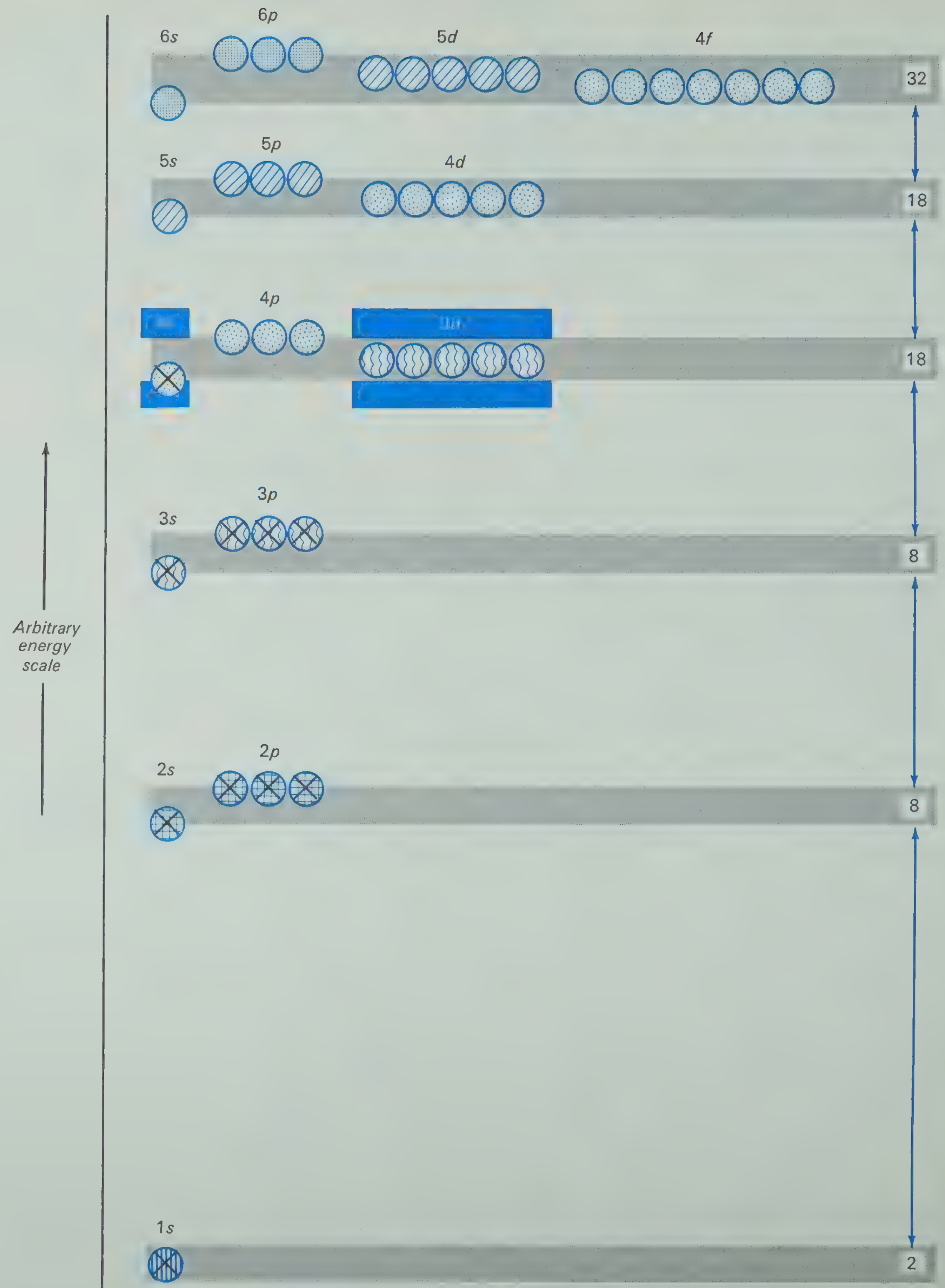

6s
6p
5d
4f
32
5s
5p
4d
18
4p
18
3s
3p
8
Arbitrary energy scale
2s
2p
8
1s
2

FIGURE 20-1

The electron configuration of calcium.

EXERCISE 20-1

Use Figure 20-1 to decide which orbital would be used after the 3*d* orbitals have been filled. What element has this configuration? In which family does this element occur?

EXERCISE 20-2

Use Figure 20-1 to decide what the electronic configuration for yttrium (Z = 39) would be. Would you expect yttrium to have chemical properties more like aluminum or scandium?

20-2 Some Properties and Regularities of the Fourth-Row Transition Elements

What trends in properties can be observed for the transition elements, scandium through zinc? What kinds of compounds do they form? How can their properties be related to the electron configurations of these elements?

All of the transition elements are metals, with high melting and boiling temperatures. They are good conductors of heat and electricity. Copper is widely used in electrical circuits because of its exceptionally high conductivity. Some of the properties of these elements are summarized in Table 20-2.

Several regularities can be observed in Table 20-2.

Molar Mass

The molar mass increases regularly across the row except for the inversion at cobalt and nickel. The molar mass of Ni might be expected to be higher than that of Co because there are more protons (28) in the Ni nucleus than in the Co nucleus (27). The reason for the inversion lies in the abundance of the naturally occurring isotopes of these elements. Natural cobalt consists entirely of the single isotope Co—59. Natural nickel consists primarily of two isotopes, Ni—58 and Ni—60, with the isotope of mass number 58 about three times as abundant as the isotope having mass number 60.

Abundance

With the exception of iron and titanium, the transition elements are not very abundant in the earth's crust. There is evidence that the center of the earth is predominantly iron and nickel. One theory for the formation of the earth suggests that the temperature rose to several thousand degrees during the early stages of development. Metals such as iron would have been present as liquids of fairly high density. These liquids would have moved toward the center of the earth. The silicate rocks which make up the outer levels of the earth's crust would have floated on the top of the liquid metals.

Melting Temperature

Except for zinc at the end of the transition element group, the melting temperatures are quite high. This is reasonable, since these elements have a large number of valence electrons and also a large number of vacant valence orbitals. Toward the end of this group of elements, the 3*d* orbitals become filled and the melting temperature is relatively low.

TABLE 20-2

Some Properties of the Fourth-Row Transition Elements

Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Molar mass, g	45.0	47.9	51.0	52.0	54.9	55.9	58.9	58.7	63.5	65.4
Abundance*, % by mass	0.005	0.44	0.015	0.020	0.10	5.0	0.0023	0.008	0.0007	0.01
Melting temperature, °C	1400	1812	1730	1900	1244	1535	1493	1455	1083	419
Boiling temperature, °C	3900	3130**	3530**	2480**	2087	2800	3520	2800	2582	907
Density, g/cm^3	2.4	4.5	6.0	7.1	7.2	7.9	8.9	8.9	8.9	7.1
First ioniz. energy, kcal/mole	154	157	155	155	171	180	180	175	176	216
2+ ion radius, Å	—	0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.72	0.74
3+ ion radius, Å	0.81	0.76	0.74	0.69	0.66	0.64	0.63	0.62	—	—
E°, volt $M \longrightarrow M^{2+} + 2e^-$	2.1***	1.6	1.2	0.90	1.18	0.44	0.28	0.25	−0.34	0.76

* In the earth's crust.
** Estimated.
*** $M \longrightarrow M^{3+} + 3e^-$

Density

The density increases in a regular manner for the transition metals, with some leveling off at Co, Ni, and Cu. This trend is closely tied to the approximately constant size of the atoms. The main effect producing density change is the increasing nuclear mass.

Ionization Energy

The ionization energies for the transition elements are rather similar in magnitude. The values are intermediate between low values for the alkali metals and high values for the noble gases. The increasing nuclear charge which tends to increase the ionization energy seems to be almost offset by the extra screening of the nucleus provided by the added electrons.

Ionic Radius

The ionic radii for the transition elements do not change appreciably from scandium to zinc. There seem to be two factors that are balanced. First, an increasing nuclear charge should pull the electrons more strongly towards the nucleus. But second, as more electrons enter the 3*d* orbitals, these electrons repel each other, increasing the size of the ion. As expected the radii for the 3+ ions are smaller than the radii of the 2+ ions.

Color

Many compounds of the transition metals and their aqueous solutions absorb light in the visible region of the spectrum. The energy levels that account for this absorption are relatively close together and involve unoccupied *d* orbitals. The environment of the ion changes the spacing of these levels, thereby influencing the color. An example is the Ni^{2+} ion, which changes from green when surrounded by water molecules to blue when ammonia is added to replace the water.

E°

The last row in Table 20-2 gives the values for the oxidation potentials for the transition metals. Except for scandium the potentials correspond to the reaction

$$M \longrightarrow M^{2+} + 2\,e^-$$

All of the elements except copper have positive $E°$ values. This means that they will dissolve in HCl solutions, liberating H_2. The negative $E°$ for copper indicates why it is one of the few elements found in the metallic state in the earth's crust. The existence of deposits of metallic copper suggests why man evolved through the Bronze Age before the Iron Age. Copper, the essential ingredient of bronze, did not require the difficult smelting process needed for iron.

EXERCISE 20-3

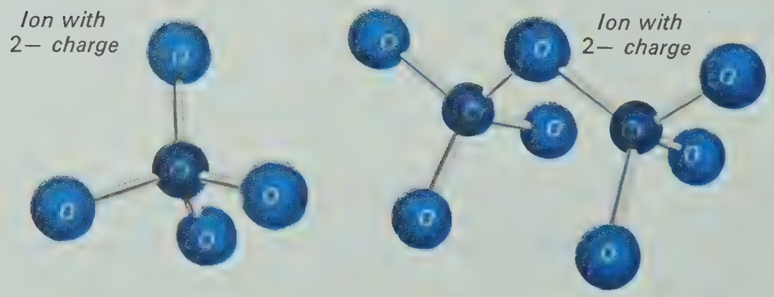
The densities for metallic K and Ca are 0.86 g/cm^3 and 1.55 g/cm^3, respectively. Use information from Table 20-2 to draw a graph of density versus atomic number for the elements K through Zn. Does your graph suggest a regularity?

20-3 Some Compounds of Chromium

Suppose we go into a chemical stockroom to see what kinds of compounds can be found for a particular transition element, chromium. First, there might be a bottle of green powder labeled Cr_2O_3, chromic oxide or chromium(III) oxide. Next to it there might be a bottle containing a red powder, CrO_3, chromium(VI) oxide. We might also find some black powder marked CrO, chromous oxide or chromium(II) oxide. There would be other compounds such as $CrCl_3$, chromic chloride, and maybe some green CrF_2, chromous fluoride. Elsewhere in the stockroom there would be bright-yellow potassium chromate, K_2CrO_4, next to a bottle of orange potassium dichromate, $K_2Cr_2O_7$. Chromium has an oxidation number of +6 in both compounds.

The anions in these last two compounds provide an interesting example of different structures containing the same oxidation number. You studied these ions and the equilibrium between them in Experiment 30. The chromate ion exhibits a tetrahedral arrangement of oxygen atoms around the central chromium ion. Dichromate may be visualized as two such tetrahedra, having one corner in common. Figure 20-2 shows the two structures. You found that chromate ion can easily be converted to dichromate ion by increasing $[H^+]$.

$$2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$



Chromate ion *Dichromate ion*

FIGURE 20-2

The structures of chromate and dichromate ions.

Returning to the stockroom search, we would conclude that chromium forms a number of stable compounds, most of them colored solids. We also would realize that chromium may have different oxidation numbers, including +2, +3, and +6, in its compounds. Similar conclusions would have resulted for most of the other transition elements. Table 20-3 summarizes some of the information chemists have found for the transition elements.

TABLE 20-3

Typical Oxidation Numbers Found for Fourth-Row Transition Elements

	Representative Compounds — Oxidation Number of Transition Element							Number of Valence Electrons in Neutral Atom	
Symbol	+1	+2	+3	+4	+5	+6	+7	3*d*	4*s*
Sc			Sc_2O_3					1	2
Ti		TiO	Ti_2O_3	TiO_2				2	2
V		VO	V_2O_3	VO_2	V_2O_5			3	2
Cr		CrO	Cr_2O_3			CrO_3 K_2CrO_4 $K_2Cr_2O_7$		5	1
Mn		MnO	Mn_2O_3	MnO_2		K_2MnO_4	$KMnO_4$	5	2
Fe		FeO	Fe_2O_3					6	2
Co		CoO	Co_2O_3					7	2
Ni		NiO	Ni_2O_3					8	2
Cu	Cu_2O	CuO						10	1
Zn		ZnO						10	2

20-4 Complex Ions

Four bottles of brightly colored solids labeled

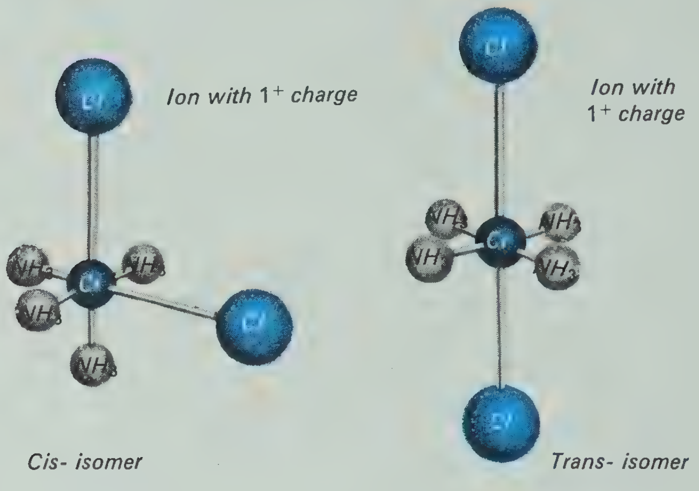
$CrCl_3 \cdot 6\,NH_3$	$CrCl_3 \cdot 5\,NH_3$	$CrCl_3 \cdot 4\,NH_3$	$CrCl_3 \cdot 3\,NH_3$
Yellow	Purple	Green	Violet

are next to each other on the stockroom shelf. The dot in the formulas simply indicates that a certain number of moles of neutral NH_3 are bound to one mole of $CrCl_3$. Chromium has an oxidation number of +3 in each compound.

This series of compounds exhibits some behavior that is not suggested by the molecular formulas. When one mole of each is dissolved in water, a solution of silver nitrate can be added in an attempt to precipitate the chloride as AgCl. The amount of chloride that can be precipitated varies from one compound to another.

Compound	Moles of Cl^- precipitated	Moles of Cl^- not precipitated
$CrCl_3 \cdot 6\,NH_3$	3	0
$CrCl_3 \cdot 5\,NH_3$	2	1
$CrCl_3 \cdot 4\,NH_3$	1	2
$CrCl_3 \cdot 3\,NH_3$	0	3

Apparently there are two ways in which chlorine is bound in these compounds. One allows chlorine to ionize and be precipitated; the other does not. In $CrCl_3 \cdot 6\,NH_3$ three Cl^- ions form and are precipitated; in $CrCl_3 \cdot 3\,NH_3$, no chloride forms. The explanation of this behavior was provided in the early 1900's by Alfred Werner. He proposed that each chromium is bonded to six neighbors. In $CrCl_3 \cdot 6\,NH_3$, the cation consists of a central Cr^{3+} surrounded by 6 NH_3 molecules at the corners of an octahedron. Octahedral geometry is illustrated in Figures 20-3 and 20-4. The three chlorine atoms form anions, Cl^-. In $CrCl_3 \cdot 5\,NH_3$, the cation consists of the central chromium ion surrounded by the five NH_3 molecules and one of the Cl^- ions. In $CrCl_3 \cdot 4\,NH_3$, the chromium is bound to four NH_3 and two Cl^-, while in $CrCl_3 \cdot 3\,NH_3$ all three Cl^- ions and three NH_3 molecules are bonded to the central Cr^{3+}. The formulas can be written in this way:



Cis- isomer

Trans- isomer

FIGURE 20-3

Structures for the isomers of $Cr(NH_3)_4Cl_2^+$.

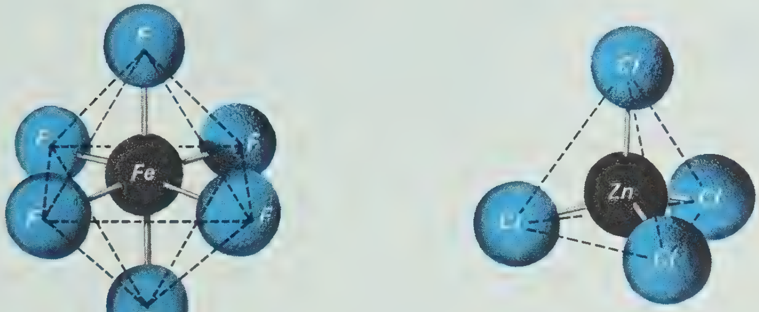
$$[Cr(NH_3)_6^{3+}]\ [Cl^-]_3$$
$$[Cr(NH_3)_5Cl^{2+}]\ [Cl^-]_2$$
$$[Cr(NH_3)_4Cl_2^{+}]\ [Cl^-]$$
$$[Cr(NH_3)_3Cl_3]$$

Werner demonstrated by experiment that only two compounds have the formula $CrCl_3 \cdot 4\,NH_3$. This is strong evidence for octahedral geometry around the central ion. Figure 20-3 shows the isomers of the cation. In one of them, the *cis*-isomer, two bonded chlorines occupy positions next to each other. In the other isomer, the *trans*-isomer, two bonded chlorines have positions on opposite sides of the metal atom.

20-5 The Geometry of Complex Ions

The way in which atoms and molecules are arranged around a central atom has a great influence on the stability of the cluster. What kinds of arrangements are found in complex ions? What shapes do they have?

First, here is a concept useful in giving spatial descriptions. The **coordination number** is the number of nearest neighbors that an atom has. For example, in the complex ion FeF_6^{3-}, each iron atom is surrounded by six fluoride ions at the corners of an octahedron. We say that the iron atom has a coordination number of 6 in this ion. In the complex ion $ZnCl_4^{2-}$, the chloride ions are arranged around a central Zn^{2+} at the corners of a regular tetrahedron. The coordination number of Zn is 4 in this ion. Figure 20-4 shows these complex ions.



FeF_6^{3-}

$ZnCl_4^{2-}$

FIGURE 20-4

Complex ions with octahedral and tetrahedral geometry.

If more than simple atoms are bound to a central atom, then the coordination number still refers to the number of nearest neighbors. For example, in $Ni(NH_3)_6^{2+}$, the cation consists of a central nickel ion joined to six ammonia molecules arranged in an octahedral manner. The nitrogen atom in each NH_3 molecule is turned toward the central nickel and the hydrogen atoms point away. This ion is shown in Figure 20-5.

The complex ion $Fe(C_2O_4)_3^{3-}$ is formed when rust stains are bleached out with oxalic acid solution. The central iron(III) ion has a coordination number of 6 even though there are only three oxalate groups around each iron. Each oxalate ion, $C_2O_4^{2-}$, uses two of its oxygen atoms to bond with the central iron atom. The number of nearest neighbors, viewed from the iron ion, is six oxygen atoms at the corner of an octahedron. A group which can furnish simultaneously two atoms for coordination is said to be *bidentate,* which literally means double-toothed. The structure for $Fe(C_2O_4)_3^{3-}$ is drawn in Figure 20-6.

In addition to the tetrahedral and octahedral structures, there are two other geometrical arrangements often found. In square planar complexes, the central atom has four near neighbors at the corners of a square. An example is the nickel cyanide anion, $Ni(CN)_4^{2-}$. In a linear complex, the coordination number is 2, corresponding to one group on each side of the central atom. When copper(I) chloride dissolves in ammonia, the complex ion $Cu(NH_3)_2^+$ forms. The structures for $Ni(CN)_4^{2-}$ and for $Cu(NH_3)_2^+$ are shown in Figure 20-7.

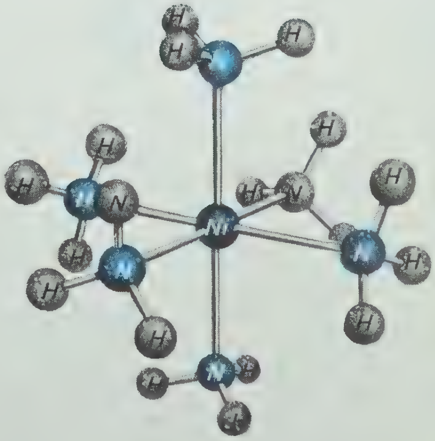


FIGURE 20-5

The geometry of $Ni(NH_3)_6^{2+}$.

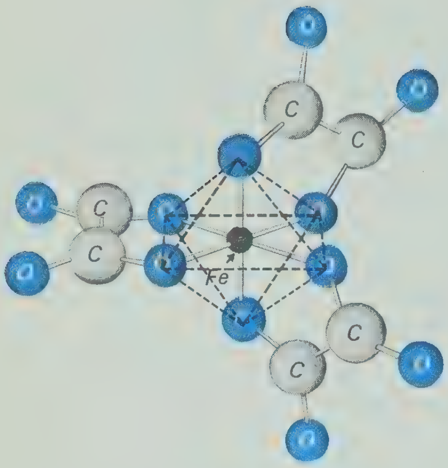
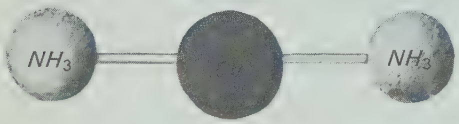
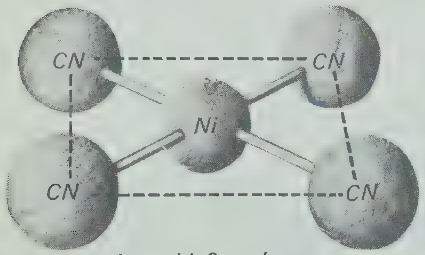


FIGURE 20-6

The structure of $Fe(C_2O_4)_3{}^{3-}$.



Ion with 1+ charge



Ion with 2− charge

FIGURE 20-7

Square planar and linear structures.

20-6 Complexes Found in Nature

Complex ions have important roles in many of the reactions that occur in plants and animals. Two of these complexes are hemin and chlorophyll. Hemin is part of hemoglobin, the pigment in red corpuscles in the blood. Chlorophyll provides the green coloring material in plants. Hemoglobin contains iron while chlorophyll is a complex compound containing magnesium. As extracted from plants, chlorophyll is made up of two closely related compounds called chlorophyll A and chlorophyll B.

The structural formula for chlorophyll A is shown on the left in Figure 20-8. The most obvious thing to notice is that chlorophyll A is a large organic molecule with a magnesium atom at the center. Around the magnesium atom there are four nearest neighbor N atoms. Each N atom is a part of a five-membered ring. The overall shape of this molecule is planar.

Hemin is shown on the right in Figure 20-8. There is an astonishing similarity between these molecules. The portions within dotted lines identify the differences between the two molecules. Except for the central metal atoms, the differences are all on the outer edges of these cumbersome molecules. We cannot help wondering how nature adopted this molecular skeleton for molecules with such different functions. We cannot avoid a feeling of impatience as we await the clarification of the possible relation, a clarification that may be provided by scientists of the next generation.

Hemoglobin carries oxygen from the lungs to the tissue cells. The iron atom of hemin forms a complex with an oxygen molecule. The connection must be a rather loose one, since O_2 is readily released to the cells. The complex is bright red, the characteristic color of arterial blood. When O_2 is stripped off the hemin group, the color changes to a purplish red, the color of blood in the veins.

Other groups can be bound to the iron atom in hemoglobin. Carbon monoxide is more firmly bound to hemoglobin than oxygen is. If we breathe a mixture of CO and O_2, the carbon monoxide molecules are picked up by the red blood cells. The sites that are normally used to carry O_2 molecules are filled by CO molecules. The tissue cells starve for lack of oxygen. If caught in time, carbon monoxide poisoning can be treated by administering fresh air or oxygen.

20-7 Iron, Workhorse of the Metals

This chapter concludes with a discussion of iron, the most commonly used of the transition elements. Iron is quite abundant. It makes up about 5% of the earth's crust, ranking fourth of all elements and second of the metals. Iron has useful mechanical properties, especially when alloyed with other elements. Steel, one of the most useful construction materials, is iron with a small percentage of carbon. Often, small amounts of other elements are added in making special types of steel.

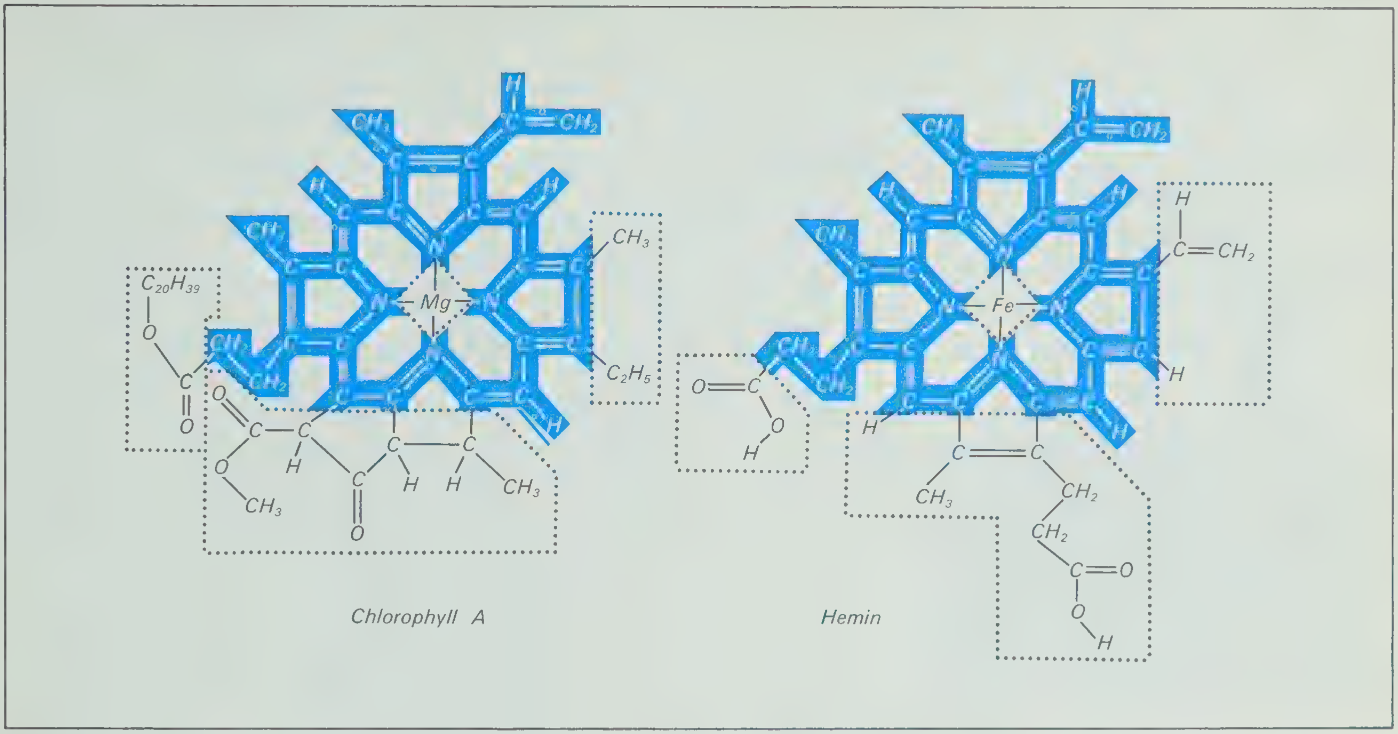


FIGURE 20-8

The structures of chlorophyll A and hemin.

The most common iron ores are the oxides hematite, Fe_2O_3, and magnetite, Fe_3O_4. The important high-grade iron ore resources in northern Michigan, Wisconsin, and Minnesota are almost depleted now. However, methods have been developed to extract iron from taconite, a very hard mixture of Fe_3O_4 in silicate rocks. One of the first steps is the concentration of Fe_3O_4, taking advantage of its magnetic properties. Other major deposits of iron oxides are found in Brazil, Venezuela, Canada, Sweden, and Russia.

Reduction of Iron Ore

The production of iron is an excellent example of chemical reduction on a massive scale. The process is carried out in a huge vertical reactor called a blast furnace. The three raw materials are iron ore, limestone, and coke. These are fed into the top of the furnace while air is blown in at the bottom. A simplified version of what goes on in a blast furnace is shown in Figure 20-9. As the mixture of ore, limestone, and coke moves down through the furnace, it encounters the updraft of oxygen. Carbon monoxide forms, and the heat energy released in this reaction maintains the high temperatures required in the furnace:

$$2\,C + O_2 \longrightarrow 2\,CO + 52.8\text{ kcal}$$

Operation		Equation	Approximate temperature
loading ore, coke, limestone		—	—
reduction	(2)	$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$	200°C
more reduction	(3)	$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$	350°C
further reduction	(4)	$FeO + CO \rightarrow Fe(s) + CO_2$	525°C
slag formation	(5) (6)	$CaCO_3 \rightarrow CaO + CO_2$ $CaO + SiO_2 \rightarrow CaSiO_3(l)$	950°C
melting		$Fe(s) \rightarrow Fe(l)$	1100°C
producing CO	(1)	$C + CO_2 \rightarrow 2CO$	1300°C
removing iron and slag ($CaSiO_3$)		—	

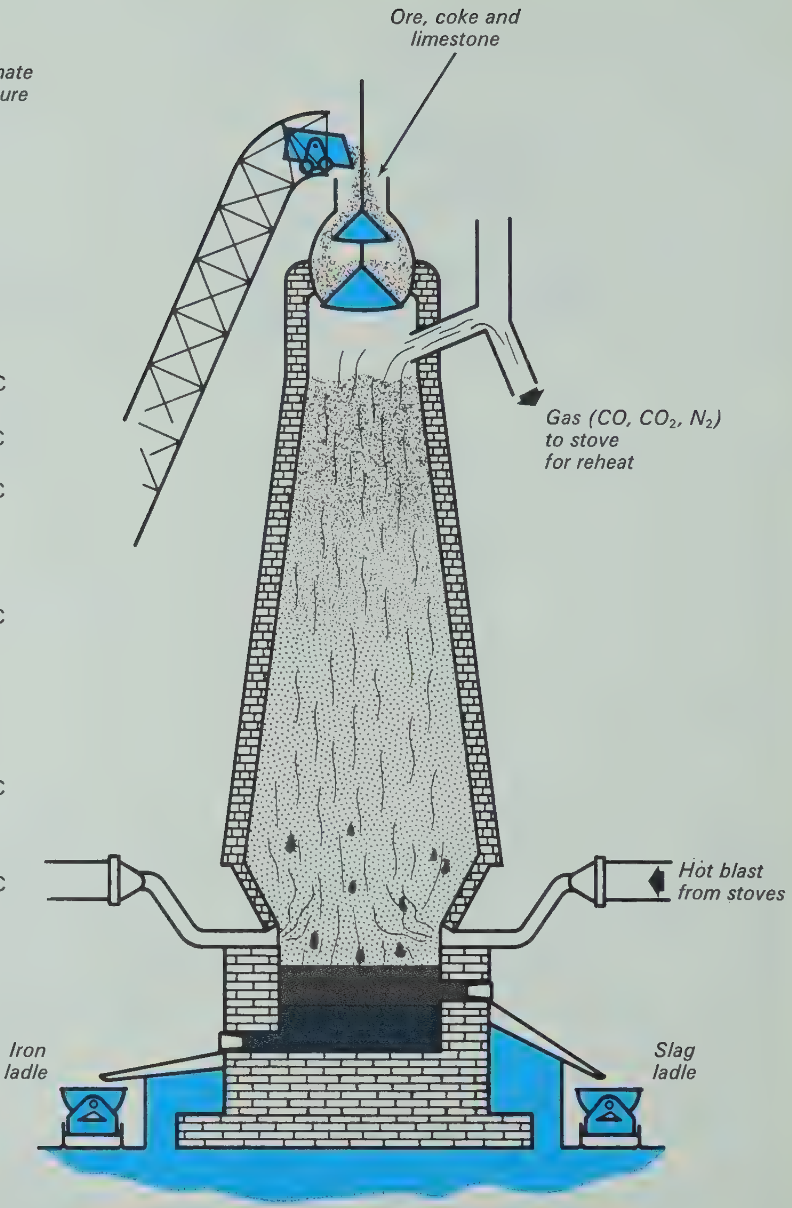

Ore, coke and limestone
Gas (CO, CO₂, N₂) to stove for reheat
Hot blast from stoves
Iron ladle
Slag ladle

FIGURE 20-9

Cross section through an operating blast furnace.

As CO rises through the furnace, the iron oxide ore is reduced to metal, probably in three stages:

$$CO + 3\,Fe_2O_3 \longrightarrow 2\,Fe_3O_4 + CO_2$$
$$CO + Fe_3O_4 \longrightarrow 3\,FeO + CO_2$$
$$CO + FeO \longrightarrow Fe + CO_2$$

The temperature near the bottom of the furnace is sufficiently high that the impure iron collects as a molten liquid. Molten slag, formed when limestone reacts with silicates in the ore, floats on top of the more dense liquid iron. An average furnace that produces about 750 tons of iron per day will also yield about 400 tons of slag. The slag is sometimes used in the manufacture of cement. About 400,000 tons of iron are produced *daily* in the United States. A general view of a blast furnace is seen in Figure 20-10.

When the iron from a blast furnace cools, it is called pig iron. The high carbon content, about 4%, makes pig iron too brittle for most uses. Pig iron is made into steel by burning out most of the carbon, sulfur, and phosphorus impurities. Manganese, vanadium, and chromium are added in small amounts to produce steel alloys with particular properties. The important stainless steel alloys contain 10–20% chromium, up to 10% nickel, and sometimes 1% manganese. Stainless steels are free from one of the main deficiencies of iron, its tendency to rust. Corrosion of iron was discussed in Section 15-8 as a very undesirable redox reaction.

Iron is so well known as the major component of steel that its use in compounds is often overlooked. Iron oxides are important as pigments and as coating for magnetic tape. The compound ferrous sulfate is widely used as an inexpensive reducing agent in a number of industrial processes.

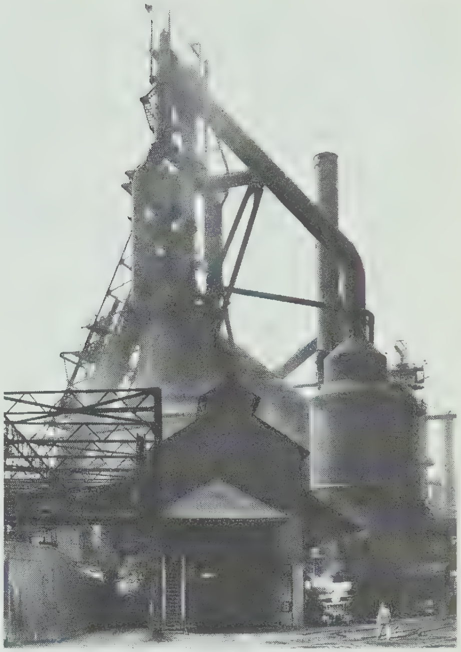


FIGURE 20-10

View of a blast furnace. (U. S. Steel Photo)

Questions and Problems for Chapter 20

1

Why are the elements with atomic numbers 21 to 30 placed in a group and considered together in this chapter?

2

Write the orbital representation for

(a) chromium,
(b) molybdenum,
(c) tungsten.

3

What properties of the transition elements are consistent with their being classified as metals?

4

Ferrous ion, iron(II), forms a complex with six cyanide ions, CN^-; the octahedral complex is called ferrocyanide. Ferric ion, iron(III), forms a complex with six cyanide ions; the octahedral complex is called ferricyanide. Write the structural formulas for the ferrocyanide and the ferricyanide complex ions.

5

Draw the different structures for an octahedral cobalt complex containing four NH_3 and two NO_2 groups.

6

Draw the structures of the compounds

$Cr(NH_3)_6(SCN)_3$
$Cr(NH_3)_3(SCN)_3$

(SCN^- is the thiocyanate ion). Consider the oxidation number of chromium to be +3 and the coordination number to be 6 in both compounds. Estimate

(a) the solubility of these compounds in water;
(b) their relative melting temperatures;
(c) the relative conductivity of the liquid phases.

7

Why does NH_3 readily form complexes, but NH_4^+ does not?

8

Place a piece of paper over Figure 9-16 and trace it. Extend the *x* axis and add the ionization energies of the transition elements. Complete the row with the following ionization energies: Ga, 138; Ge, 187; As, 242; Se, 225; Br, 273; Kr, 322; Rb, 96 kcal/mole.

9

Chromic oxide, Cr_2O_3, is used as a green pigment and is often made by the reaction between $Na_2Cr_2O_7$ and NH_4Cl to give Cr_2O_3, NaCl, N_2, and H_2O. Write a balanced equation and calculate how much pigment can be made from 1.0×10^2 kg of sodium dichromate.

10

What is the oxidation number of manganese in each of the following: MnO_4^-; Mn^{2+}; Mn_3O_4; MnO_2; $Mn(OH)_2$; $MnCl_2$; MnF_3?

11

Manganese(III), Mn^{3+}, spontaneously disproportionates to Mn^{2+} and MnO_2. Balance the equation for the reaction which occurs in aqueous solution.

12

Use the $E°$ values in Table 20-2 to predict what might happen if a piece of iron is placed in a 1 *M* solution of Mn^{2+} and if a piece of manganese is placed in a 1 *M* solution of Fe^{2+}. Balance the equation for any reaction that you feel would occur to an appreciable extent.

13

Iron exists in one cubic crystalline form at 20°C (body-centered cubic, with cube edge length 2.86 Å) and in another form at 1100°C (face-centered cubic, with cube edge length 3.63 Å).

(a) Draw a picture of each unit cell, showing the nine atoms involved in a body-centered cubic cell and the fourteen atoms involved in a face-centered cubic cell. (See Figures 17-20 and 17-21.)
(b) Decide the number of unit cells with which each atom is involved (in each structure).
(c) How many atoms are in each unit cell if we take into account that some atoms are shared by two or more adjoining unit cells?
(d) Calculate the volume of the unit cell and, with your answer to part (c), the volume per atom (for each structure).
(e) What conclusion can be drawn about the "effective size" of an iron atom?

14

One of the important cobalt ores is

$Co_3(AsO_4)_2 \cdot 8\ H_2O$

How much of this ore is needed to make 1.0 kg of Co?

15

Nickel carbonyl, $Ni(CO)_4$, boils at 43°C, and uses the sp^3 orbitals of Ni for bonding. Give reasons to justify the following:

(a) it forms a molecular solid;
(b) the molecule is tetrahedral;
(c) bonding to other molecules is of the van der Waals type;
(d) the liquid is a nonconductor of electricity;
(e) it is not soluble in water.

16

Write balanced equations to show the dissolving of $Cu(OH)_2(s)$ on the addition of $NH_3(aq)$, and also the reprecipitation caused by the addition of an acid.

17

Cupric sulfide, copper(II) sulfide, reacts with hot nitric acid to produce nitric oxide gas, NO, and elemental sulfur. Sulfur and nitrogen are the only elements whose oxidation numbers change. Write the balanced equation for the reaction.

Radioactivity and Nuclear Changes

21

Becquerel discovered, in 1896, that uranium compounds had the unusual property of releasing energy spontaneously. Soon a number of scientists began to carry out experiments in their search for an explanation of this new phenomenon. The observation that some uranium ores had much higher levels of "radioactivity" than purified uranium compounds suggested that there might be new elements in those ores that were more radioactive than uranium. Marie Curie and her husband Pierre were the first to show that this indeed was true.

The method used by the Curies was relatively simple but at the same time very exacting. After dissolving the ore, different precipitating agents were added to the solution. In some instances the radioactive elements would concentrate in the precipitate. In other operations, the radioactivity would remain in solution. The first element discovered by the Curies was similar in its chemical behavior to tellurium. The name *polonium* was chosen for this element, and it was placed below tellurium in the Periodic Table. The other element to be isolated by the Curies was *radium.* Radium showed chemical behavior like that of barium. Only after many fractional crystallizations was radium bromide separated from barium bromide. Radium was placed below barium in the second column of the Periodic Table.

Other scientists carried out similar investigations with different ores and, soon, the Periodic Table became overcrowded. Several different samples exhibited the chemical behavior of radium but had quite different radioactive properties. A rather strange dilemma confronted scientists! Neither Dalton's Atomic Theory nor Mendeleev's Periodic Table predicted such behavior. Dalton had proposed that elements were made up of atoms that were identical in all respects. Mendeleev had arranged the elements so that each had its own place in the Periodic Table. How, then, could the place for radium be shared by several "kinds" of radium?

The confusion was resolved by the suggestion that elements might be composed of different kinds of atoms called *isotopes.* This chapter will start with the discussion of the experiments that led to an understanding of isotopes and of radioactivity.

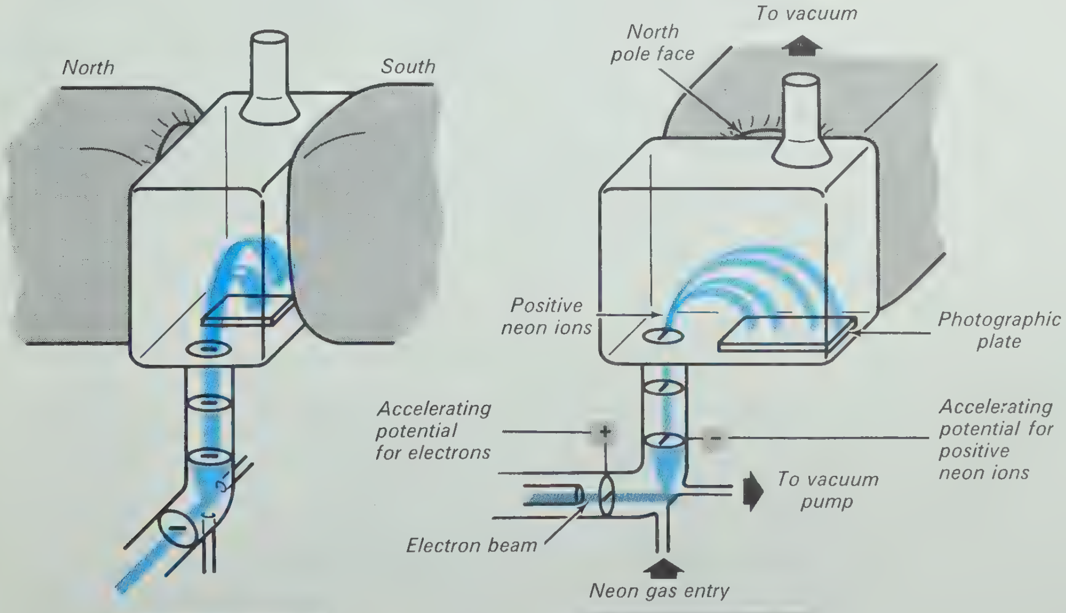
21-1 The Mass Spectograph and Isotopes

Thomson's experiments (Sections 8-2 and 8-3) allowed him to measure the charge-to-mass ratio for the ions in gas discharge tubes. The same value for e/m was always found for ions with negative electric charge. The e/m ratio was independent of the gas in the tube. For ions with positive electric charge, the values for e/m varied from one gas to another. After Millikan had measured e, the charge of the electron, Thomson's e/m ratios made it easy to calculate the mass of the positive ions. Since his experiments separated ions according to mass, the instrument he used was referred to as a *mass spectrograph.*

One type of mass spectrograph is shown schematically in Figure 21-1. Positive ions are accelerated through a slotted negative electrode and then passed through a uniform magnetic field. The left view in Figure 21-1 shows the apparatus supported between the pole faces of a strong magnet. The right view is an enlargement of the spectrograph rotated so that the magnetic field is directed perpendicular to the page.

Although positive ions can be produced in a gas discharge tube, it is more convenient to bombard the gas with an electron beam. If the bombarding electrons have enough energy, positive ions form when electrons interact with gas molecules. In Figure 21-1, neon gas enters at the bottom of the apparatus. As the gas passes through the electron beam, some atoms absorb energy and then lose electrons to form neon ions, Ne^{+} and Ne^{2+}. These ions are accelerated and pass through the slotted electrode. While

FIGURE 21-1 A mass spectrograph analyzing a neon sample.


North
South
To vacuum
North pole face
Positive neon ions
Photographic plate
Accelerating potential for electrons
+
−
Accelerating potential for positive neon ions
To vacuum pump
Electron beam
Neon gas entry

a. View perpendicular to magnetic field

b. View along direction of magnetic field each positive ion is in the magnetic field, it follows a circular path fixed by its mass, speed, and charge. For ions of the same speed, a large mass leads to a large radius for the circle; a large charge leads to a small radius. After circling through an arc of 180°, the ions strike a photographic plate. The impact of the ions causes a reaction that leads to a darkening of the plate. A line occurs for each ion at a position determined by the charge-to-mass ratio. Measurement of the position of each line permits calculation of the mass of the ion. The record on the photographic plate is called a *mass spectrum.*

The mass spectrum for neon consists of two widely separated groups of lines. The lines corresponding to large radii are caused by neon ions with a single positive charge while the lines corresponding to small radii are caused by doubly charged ions. For each ionic charge there are two slightly separated lines which indicate that neon consists of atoms with different masses. The relative abundance of these atoms can be determined by measuring the intensity of the lines caused by each ion beam.

Thomson's experiments demonstrated that the element neon contained at least two kinds of atoms. One had a molar mass of approximately 20 grams, and the other approximately 22 grams. The line corresponding to mass 20 is about ten times as intense as that for mass 22. In a more refined instrument, a third line for mass 21 can be detected, but its intensity is about three percent of the already weak mass 22 line. The best mass spectrometers in use today can determine masses to a precision better than one part in a billion!

The dilemma of several kinds of atoms occupying the same place in the Periodic Table was resolved. In the current model the dense nucleus contains protons and neutrons. The position in the Periodic Table is determined by the number of protons, Z, which is also the atomic number for the element. The chemical behavior of an element is primarily determined by the nuclear charge, and only in minor ways by the nuclear mass. The **mass number** (**A**) for an atom is the sum of the number of protons (Z) and the number of neutrons (N) in the nucleus. The notations

$$^{20}_{10}\mathrm{Ne} \qquad \text{and} \qquad ^{22}_{10}\mathrm{Ne}$$

represent the two kinds of neon atoms that Thomson measured. Each contains the same number of protons. The name *isotope* was coined to refer to atoms that have the same number of protons but different numbers of neutrons. It is customary to write the atomic number at the lower left of the chemical symbol and the mass number at the upper left of the symbol. One isotope of neon has 10 protons and 10 neutrons in the nucleus; another isotope has 10 protons and 12 neutrons.

EXERCISE 21-1

When chlorine, Cl_2, is examined in a mass spectrograph, Cl_2^+, Cl^+, and Cl^{2+} ions are formed. Remembering that there are two isotopes of chlorine, $^{35}_{17}Cl$ (75%) and $^{37}_{17}Cl$ (25%), describe qualitatively the appearance of the mass spectrum. Which ion will produce lines at the largest radius? Which at the smallest radius? How many lines will each type of ion produce?

EXERCISE 21-2

Suppose a mass spectrograph is used to measure the charge/mass ratio for fluorine ions. Fluorine has only one stable isotope and its molar mass is 19.0 grams/mole. From the measured charge/mass ratio, 5.08×10^3 coulombs/gram, and the assumption that the ion has one electron charge, calculate the mass of one ion. Use $e = 1.6 \times 10^{-19}$ coulomb. Repeat the calculation, assuming the ion has two electron charges. Now calculate Avogadro's number from the mass of a mole of fluorine ions, using each of your two calculations. Which assumption about ion charge do you prefer? Could the other be correct as well?

21-2 Nuclear Changes

Before we investigate the phenomenon of radioactivity, let us consider the possibility of reactions in which nuclei can be altered. These reactions change the number of protons and neutrons in the nucleus. This study will reveal some marked differences between chemical and nuclear reactions and will introduce a notation that will be useful throughout the rest of this chapter. We have already started the notation with $^{20}_{10}Ne$ and $^{22}_{10}Ne$ in the preceding section.

The fact that nuclei remain intact during chemical reactions suggests that much larger energies are required for nuclear changes than for chemical changes. Experimentally, this proves to be true. Nuclear reactions usually involve energy changes over a million times greater than those we find in chemical reactions. This enormous factor accounts for the current interest in nuclear reactions as a source of energy.

One such nuclear reaction is represented by the equation

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\ ^{1}_{0}n + \text{energy}$$

Before we examine the details of this rather strange looking equation, let us focus our attention on the "+ energy" term. The numerical value is of the order of 4.5×10^9 kcal/mole of uranium. Look at that figure again and compare it to the molar heat of combustion of carbon. Roughly, what is the ratio of these two energies? It is 10^7, or 10 million!

Now examine the reaction in more detail. Forget momentarily the subscripts and superscripts. Recall from Chapter 8 that the neutron (n) is one of the fundamental particles visualized as present in nuclei. What has happened?

$$\mathrm{U} + n \longrightarrow \mathrm{Ba} + \mathrm{Kr} + 3n$$

Instead of producing new kinds of substances by combination of atoms, the element uranium has combined with a neutron and as a result has split into two other elements—barium and krypton—plus three more neutrons. Atoms of a given element are characterized by their atomic number, the number of units of positive charge on the nucleus. For one element to change into another element the nucleus must be altered. In our example the uranium nucleus, as a result of reacting with a neutron, splits or fissions into two other nuclei and releases, in addition, neutrons.

A glance at the Periodic Table will show that the subscripts we have attached to our symbols are the atomic numbers of the elements designated by the symbols—92 for U, 56 for Ba, 36 for Kr. The zero subscript attached to the neutron denotes the lack of charge on this particle. If we look at the subscripts,

$${}_{92}\mathrm{U} + {}_{0}n \longrightarrow {}_{56}\mathrm{Ba} + {}_{36}\mathrm{Kr} + 3\ {}_{0}n$$

we notice that their sum on each side of the equation is identical:

$$92 + 0 = 56 + 36 + (3 \times 0)$$

This identity is but another way of expressing the law of conservation of charge.

In the model of nuclear structure you were given in Chapter 8, the nucleus was pictured as being built up of protons and neutrons. These two kinds of particles are given the general name **nucleon.** The ***mass number*** *of a nucleus is equal to the number of nucleons present.* The superscripts in our equation are mass numbers:

$${}^{235}\mathrm{U} + {}^{1}n \longrightarrow {}^{141}\mathrm{Ba} + {}^{92}\mathrm{Kr} + 3\ {}^{1}n$$

Apparently the mass numbers are also conserved:

$$235 + 1 = 141 + 92 + (3 \times 1)$$

We can rephrase this in the form of a rule: *The total number of nucleons is unchanged during nuclear reactions.*

EXERCISE 21-3

According to the model developed in Chapter 8, how many nucleons are present in a uranium nucleus of mass number 235? How many protons are present? How many neutrons?

Actually, then, by our symbol $^{235}_{92}\mathrm{U}$ we are representing not an atom, but a **nuclide,** a particular nuclear species of given mass number (A) and atomic number (Z). Our equation is written in terms of nuclides and particles associated with them. This nuclear equation tells us nothing about what compound of uranium was bombarded with neutrons or what compound of barium is formed. It summarizes only the *nuclear changes.* During the nuclear change there is much disruption of other atoms because of the tremendous amounts of energy liberated. We do not know in detail what happens, but eventually electrically neutral substances (chemical compounds) result and the neutrons are consumed by other nuclei.

It is easy to determine that there is an electron balance between the reactants and products:

	Reactants		Products		
Nucleus	$_{92}\mathrm{U}$	$_{0}n$	$_{56}\mathrm{Ba}$	$_{36}\mathrm{Kr}$	$3\ _{0}n$
Electrons associated with nucleus	92	0	56	36	0

$$92 = 56 + 36 = 92$$

Note one other characteristic of the particular nuclear reaction we have been examining. *Atoms are not conserved.* This statement applies to many nuclear reactions.

Now that the notation is established, let us return to a type of nuclear change which occurs spontaneously: radioactive decay.

21-3 Radioactive Decay

Early studies of natural radioactivity identified three forms of energy release, called alpha, beta, and gamma emission. Table 21-1 summarizes the characteristics of each radioactive decay process.

TABLE 21-1

Radioactive Rays

Name	Charge	Approximate Molar Mass, grams	Speed after Emission (c = speed of light)	Description	Penetrating Power
α alpha	2+	4	$\sim 0.05c$	Nucleus of helium atom $^{4}_{2}\mathrm{He}$	Short range, high ionization per centimeter
β beta	1−	$\frac{1}{1837}$	$0.3-0.99c$	Electron $_{-1}^{0}e$	Intermediate range; intermediate ionization per centimeter
γ gamma	0	0	c	High energy photons	Long range; little ionization per centimeter

All three of these rays are emitted by a pure uranium compound or by a piece of uranium ore. It was a triumph of careful experimentation to demonstrate that there were many radioactive elements in the ore or in the supposedly pure compound. Eventually these elements were separated and studied in detail by techniques similar to those used by the Curies.

Rutherford and Soddy demonstrated that an element which emitted an alpha particle spontaneously changed into another element (called a daughter element) whose atomic number was two less than the parent and whose mass number was four less. The daughter element fits in the Periodic Table two places to the left of the parent element. For one of the isotopes of radium found in uranium ores we can write

$$^{226}_{88}\text{Ra} \longrightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$

A consideration of the electron balance shows that two electrons are available to combine with the alpha particle ($^{4}_{2}$He—helium nucleus of charge 2+) to form helium atoms. Gaseous helium is a product of alpha-emitting radioactive materials.

The same two scientists also found that beta emission corresponded to the spontaneous decay of an element into a daughter element whose mass number remained constant but whose atomic number increased by one. The daughter element is a member of the group in the Periodic Table one place to the right of the parent element. For one of the isotopes of thorium found in uranium ore we can write

$$^{234}_{90}\text{Th} \longrightarrow {}^{0}_{-1}e + {}^{234}_{91}\text{Pa}$$

Since a new atom (protactinium) is produced, the electron (beta particle) must have come from the nucleus of the thorium atom. The protactinium atom with the increased atomic number requires this extra electron to achieve electron balance.

The question of how a thorium nucleus, built of 90 protons and 144 neutrons, emits an electron did not bother Rutherford and Soddy because they used a model which pictured the nucleus as containing 234 protons and 144 electrons. Today in terms of our proton-neutron model we say that the following takes place:

$$^{1}_{0}n \longrightarrow {}^{1}_{1}p + {}^{0}_{-1}e + \text{neutrino}$$

We will not study the neutrino in this textbook.

Gamma rays (high-frequency electromagnetic radiation) accompany alpha and/or beta emissions.

The details of the many steps whereby $^{238}_{92}$U decays into the stable isotope $^{206}_{82}$Pb are shown in Figure 21-2. These steps are called a *radioactive decay series* and will be studied in more detail in Section 21-7. Two other natural radioactive decay series are known. They involve the decay of $^{232}_{90}$Th into $^{208}_{82}$Pb and the change of $^{235}_{92}$U into $^{207}_{82}$Pb.

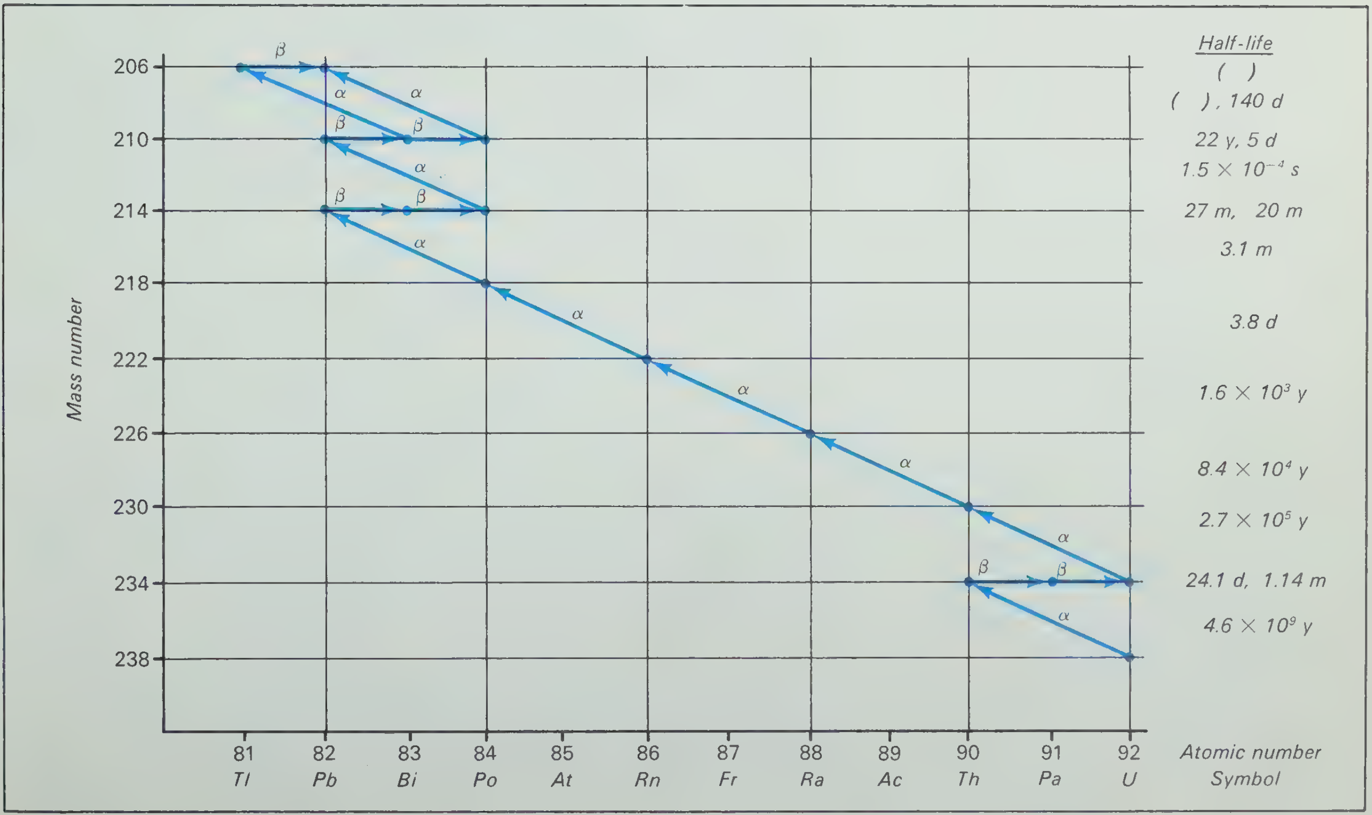
An important characteristic of all radioactive species is that in a specified period of time a constant fraction of the nuclei decompose. Normally the time for one half of the nuclei to decay is chosen. This length of time, $T_{1/2}$, is known as the **half-life** of the nuclide. Thus, if we start with one gram of material whose half-life is 20 minutes, the following observations could be made:

During 20 minutes
$\frac{1}{2}$ gram would decay; $(1 - \frac{1}{2}) = \frac{1}{2}$ gram would be left.
During another 20 minutes (or 40 minutes total)
$(\frac{1}{2})(\frac{1}{2}$ gram) or $\frac{1}{4}$ gram would decay; $(\frac{1}{2} - \frac{1}{4}) = \frac{1}{4}$ gram would remain.
During still another 20-minute period (or 60 minutes total)
$(\frac{1}{2})(\frac{1}{4}$ gram) or $\frac{1}{8}$ gram would decay; $(\frac{1}{4} - \frac{1}{8}) = \frac{1}{8}$ gram would be left.

The rate of decay of any radioactive species is shown in Figure 21-3, expressed in terms of its half-life.

The half-lives of various elements vary widely. For the alpha decay of $^{238}_{92}U$ into $^{234}_{90}Th$, the half-life is 4.5×10^9 years. During 24.1 days, half of a $^{234}_{90}Th$ sample decomposes by beta decay. Half-lives as short as microseconds have been observed. Note that the alpha decay of $^{226}_{88}Ra$ mentioned on page 416 is part of the $^{238}_{92}U$ decay series shown in Figure 21-2. $^{226}_{88}Ra$ has a half-life of 1620 years. Since the age

FIGURE 21-2 Radioactive decay series $^{238}_{92}U \longrightarrow {}^{206}_{82}Pb$.


Half-life
( )
( ), 140 d
22 y, 5 d
1.5×10^{-4} s
27 m, 20 m
3.1 m
3.8 d
1.6×10^3 y
8.4×10^4 y
2.7×10^5 y
24.1 d, 1.14 m
4.6×10^9 y
Mass number
206
210
214
218
222
226
230
234
238
α
β
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
89 Ac
90 Th
91 Pa
92 U
Atomic number
Symbol

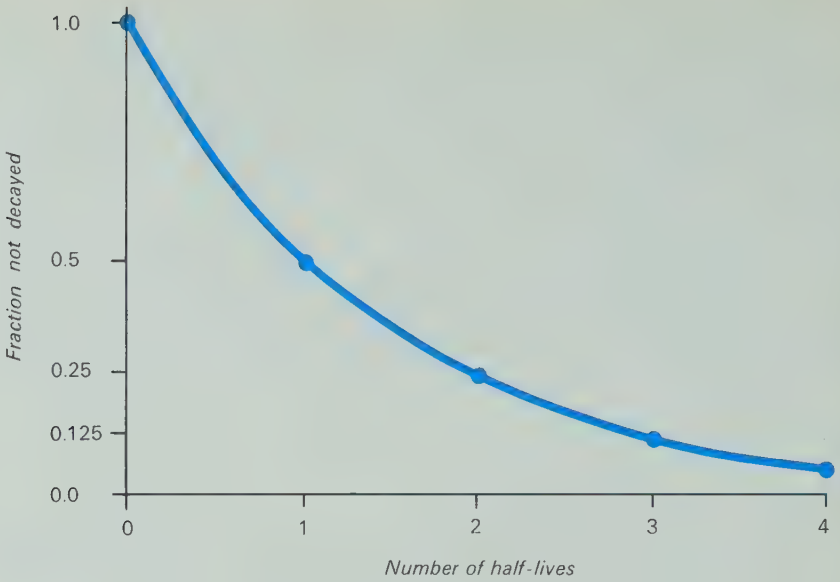


FIGURE 21-3

Radioactive decay.

of the earth is known to be about 5 × 10^9 years, it is easy to understand why $^{238}_{92}U$ is found in the earth's crust. On the other hand, $^{226}_{88}Ra$ would have disappeared soon after the earth's formation except that it is supplied continuously through the decay of $^{238}_{92}U$.

21-4 Nonspontaneous Nuclear Reactions

Rutherford was the first one to show that nonspontaneous nuclear reactions induced by collision or bombardment could occur. After many years of careful experiments, he was able to prove in 1919 that an alpha particle with enough energy can combine with a nucleus instead of just being scattered by it. He showed that this reaction had occurred:

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$$

The alpha particle with its 2+ charge had to overcome the very high coulombic *repulsion* forces surrounding the nitrogen nucleus with its 7+ charge. The probability of this occurring is very low. Once the alpha particle gets very close to the nitrogen nucleus, strong *attractive* nuclear forces take over. The exact nature of nuclear forces is still not known. But the fact that protons and neutrons do not spontaneously repel each other enough to destroy the nucleus means that some attractive forces are present.

During the fifty years since Rutherford identified this nuclear reaction, many others have been studied. With the advent of the high-energy accelerating machines such as the cyclotron, chemists and physicists have explored a variety of nuclear reactions. Figure 21-4 shows schematically the energy situation near a nucleus when a charged alpha particle or an uncharged neutron approaches

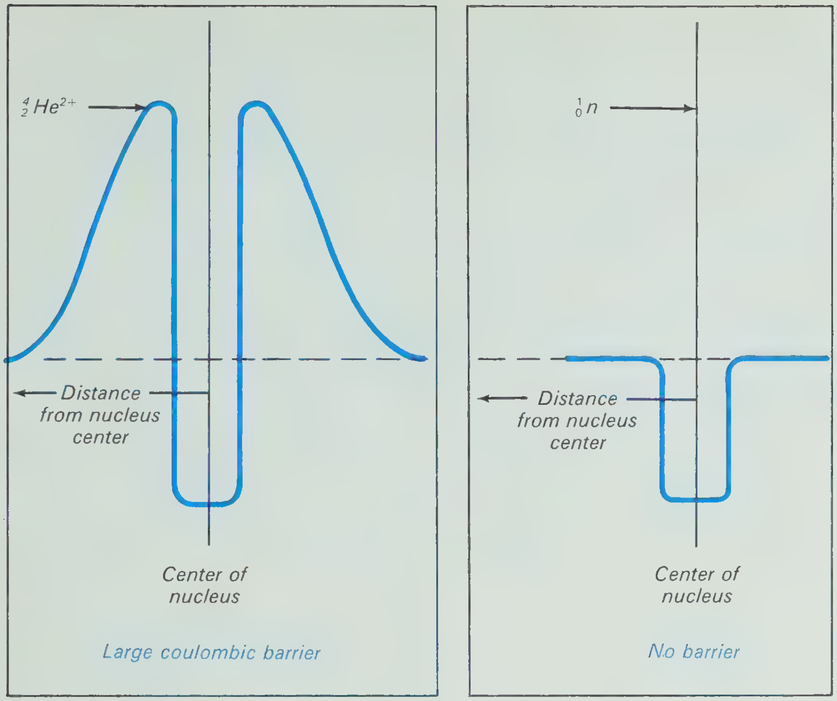

$^{4}_{2}He^{2+}$
Distance from nucleus center
Center of nucleus
Large coulombic barrier
$^{1}_{0}n$
Distance from nucleus center
Center of nucleus
No barrier

FIGURE 21-4

Energy barriers for nuclear reactions using α particles or neutrons.

the nucleus. Neutron reactions occur with much higher probability because no coulombic repulsion occurs.

Let us look at a few examples of nuclear changes induced by bombardment and some of the new particles discovered. In 1930, Cockroft and Walton accelerated protons so that they had enough energy to penetrate the coulombic barrier of the $^{7}_{3}Li$ nucleus. Helium was produced, as represented by

$$^{1}_{1}H + ^{7}_{3}Li \longrightarrow 2\,^{4}_{2}He$$

In the same year, a penetrating radiation was observed when beryllium compounds were bombarded with alpha particles. Chadwick interpreted the radiation by the reaction

$$^{4}_{2}He + ^{9}_{4}Be \longrightarrow ^{1}_{0}n + ^{12}_{6}C$$

and thus the *neutron* was discovered.

In 1932, Anderson was studying cosmic rays and found evidence for a particle like the electron but positively charged. He named it the *positron,* or positive electron ($_{+1}^{0}e$). Soon others showed that the positron was emitted by a nitrogen isotope formed by the reaction

$$^{4}_{2}He + ^{10}_{5}B \longrightarrow ^{1}_{0}n + ^{13}_{7}N$$

The $^{13}_{7}N$ nuclide is radioactive and decays spontaneously according to

$$^{13}_{7}N \longrightarrow _{+1}^{0}e + ^{13}_{6}C$$

Radioactivity induced by bombardment is known as *artificial radioactivity.* Hundreds of artificially radioactive nuclides have been produced.

The nuclear reaction in Section 21-2 is known as a *fission* reaction. Another is

$$^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{90}_{38}\text{Sr} + {}^{143}_{54}\text{Xe} + 3\,{}^{1}_{0}n$$

This type of reaction is used in atomic piles or occurs in the atom bomb. There are some fifty pairs of products known, including lanthanum and bromine or cerium and selenium. Each pair is such that the sum of their atomic numbers is 92.

The hydrogen bomb depends on *fusion* processes. A typical one is

$$^{2}_{1}\text{H} + {}^{2}_{1}\text{H} \longrightarrow {}^{3}_{2}\text{He} + {}^{1}_{0}n$$

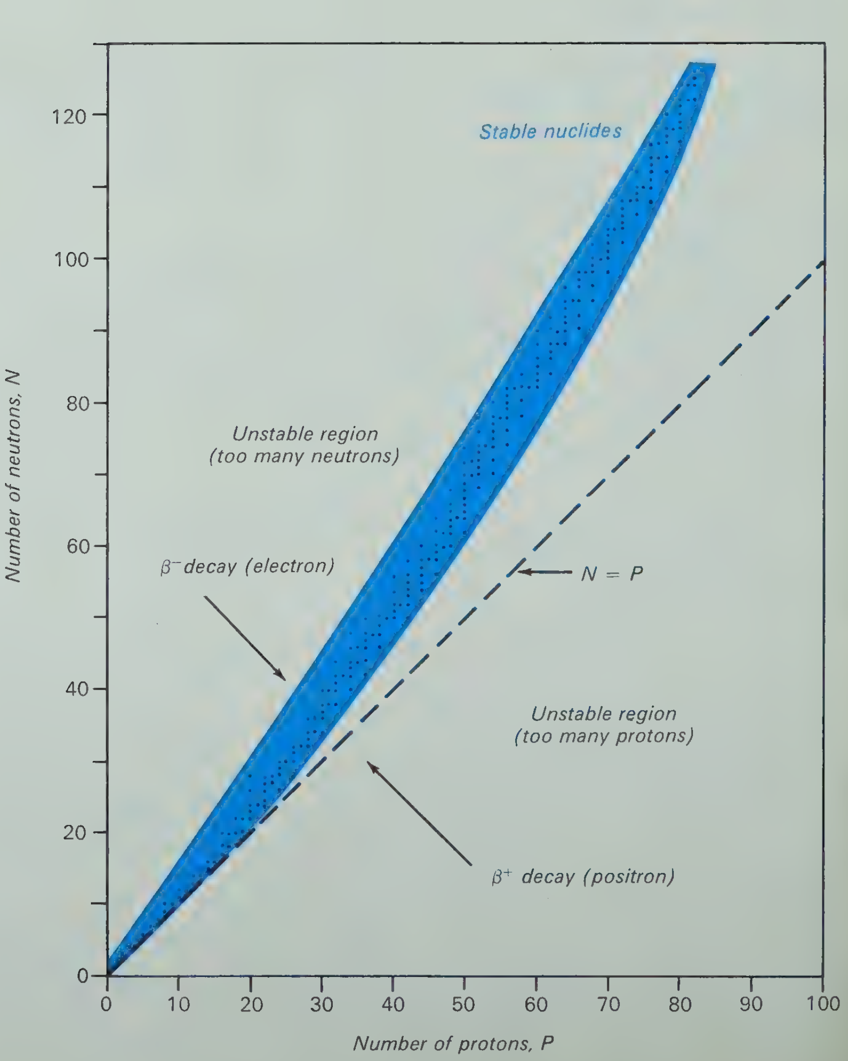


FIGURE 21-5

Nuclear stability.

To overcome the repulsive force as the two hydrogen nuclei approach each other, their collision energy must be of the order of 5×10^5 kcal/mole. Such kinetic energies are achieved when the temperature is around 200 million degrees Kelvin. At this temperature any gas is a collection of nuclei, ions, and electrons. Gas in this state is known as a **plasma.**

All the man-made elements beyond atomic number 92 (the trans-uranium elements) were synthesized by bombardment reactions. For example, element 98, californium (Cf, Z = 98), is formed from ${}^{238}_{92}U$ and ${}^{12}_{6}C$ nuclides:

$${}^{238}_{92}U + {}^{12}_{6}C \longrightarrow {}^{246}_{98}Cf + 4\,{}^{1}_{0}n$$

21-5 Nuclear Stability

Some combinations of neutrons and protons lead to stable nuclides. Other combinations of neutrons and protons lead to unstable or radioactive nuclides. In Table 21-2, the isotopes of carbon are listed; ${}^{12}_{6}C$ and ${}^{13}_{6}C$ are stable while ${}^{10}_{6}C$, ${}^{11}_{6}C$, ${}^{14}_{6}C$, and ${}^{15}_{6}C$ are radioactive.

TABLE 21-2

Carbon Isotopes

Nuclide Symbol	Number of Protons	Number of Neutrons	Type of Decay	Half-life $T_{1/2}$
${}^{10}_{6}C$	6	4	Positron (${}^{0}_{+1}e$) or β^+	19 seconds
${}^{11}_{6}C$	6	5	Positron (${}^{0}_{+1}e$) or β^+	20 minutes
${}^{12}_{6}C$	6	6	Stable	—
${}^{13}_{6}C$	6	7	Stable	—
${}^{14}_{6}C$	6	8	Beta (${}^{0}_{-1}e$) or β^-	5570 years
${}^{15}_{6}C$	6	9	Beta (${}^{0}_{-1}e$) or β^-	2.4 seconds

Stable nuclei with low mass tend to have approximately equal numbers of protons and neutrons. As the mass increases, stable nuclides have more than one neutron per proton. In Figure 21-5 each stable nuclide is represented by a dot in the blue region.

Unstable nuclei achieve stability by radioactive decay. Here are two sets of sample reactions; first, a beta decay:

$${}^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e \text{ (beta particle)}$$

To create the ${}^{14}_{7}N$ nucleus, the seventh proton is produced by this reaction:

$${}^{1}_{0}n \longrightarrow {}^{1}_{1}H + {}^{0}_{-1}e$$

The second example illustrates positron decay:

$$^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}e \text{ (positron)}$$

In making the $^{11}_{5}\text{B}$ nucleus, a proton is converted to a neutron by emitting a positron:

$$^{1}_{1}\text{H} \longrightarrow {}^{1}_{0}n + {}^{0}_{+1}e$$

In this part of the universe, electrons are stable, but positrons disappear by reaction with electrons soon after they are created. The equation for this matter-antimatter reaction is

$$^{0}_{-1}e + {}^{0}_{+1}e \longrightarrow \gamma \text{ radiation}$$

The stability of a nuclide depends on its neutron/proton ratio. Even among those nuclei that are considered stable, however, there is a variation in the forces which hold the nucleons together. In order to study this variation in nuclear binding energy, consider the process of building a nucleus from protons and neutrons, for example, the hypothetical reaction

$$2\,{}^{1}_{1}\text{H} + 2\,{}^{1}_{0}n \longrightarrow {}^{4}_{2}\text{He}$$

First compare the masses of the reactants with those of the product:

Mass of 2 protons	= 2 × 1.00759	= 2.01518 g/mole
Mass of 2 neutrons	= 2 × 1.00897	= 2.01794 g/mole
Total mass of reactants		= 4.03312 g/mole
Mass of $^{4}_{2}\text{He}$ produced		= 4.00277 g/mole
Mass difference between products and reactants		0.03035 g/mole

There is a decrease of 0.03035 gram per mole of helium nuclei formed in this reaction. An equivalent amount of energy is released. The Einstein mass-energy relationship is given in the equation $E = mc^2$. In the formation of 1 mole of helium nuclei there would be

$$E = mc^2 = \left(0.03\,\frac{\text{g}}{\text{mole}}\right) \times \left(3 \times 10^{10}\,\frac{\text{cm}}{\text{sec}}\right)^2$$

$$= 2.7 \times 10^{19} \text{ ergs/mole}$$

$$E = (2.7 \times 10^{19} \text{ ergs/mole}) \times (2.4 \times 10^{-11} \text{ kcal/erg})$$

$$= 6.4 \times 10^{8} \text{ kcal/mole}$$

or 640 million kilocalories of energy released. This amount of energy can be considered as the binding energy of a mole of helium nuclei. This much energy must be supplied to dissociate a mole of $^{4}_{2}\text{He}$ nuclei into two moles each of protons and neutrons. Binding energy between nucleons in nuclides corresponds to bonding energy between atoms in molecules. Of course, the energy is millions of times greater for nucleon binding.

Similar calculations can be made for other nuclides. A significant comparison between nuclear binding energies is seen if the total binding energy of each nuclide is divided by the number of nucleons in the nucleus. This calculation gives the binding energy per particle in a mole of nuclei. The binding energy per particle varies in a systematic way as the mass number of the nucleus increases. This variation is shown in Figure 21-6.

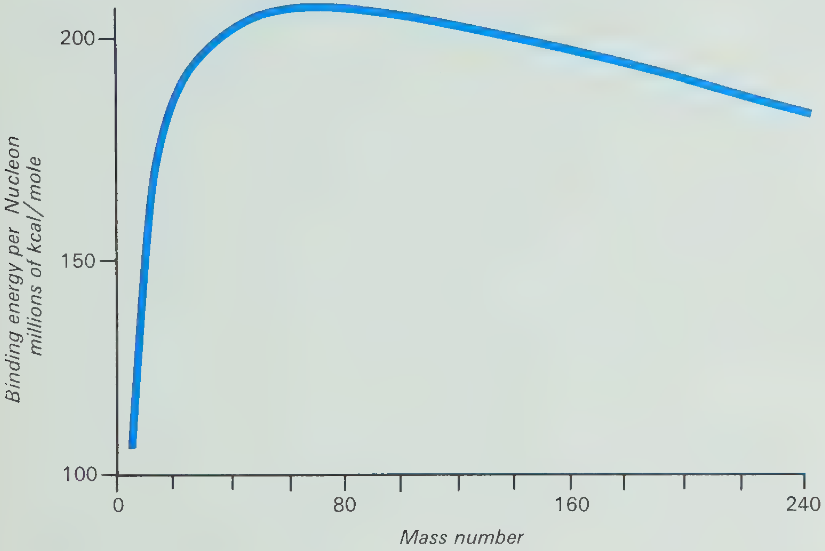


FIGURE 21-6

The binding energy per particle in the nucleus.

The nuclei that have a mass number of approximately 60 have the highest binding energy per nuclear particle and are therefore the most stable nuclei. This graph helps us to understand the existence of the processes of nuclear fission and nuclear fusion. If a nucleus of the heavier elements such as uranium and plutonium is split into two smaller fragments, the binding energy per nucleon is greater in the lighter nuclei. As in every other reaction in which the products are more stable than the reactants, energy is evolved by this process of nuclear fission. Generally this fission reaction is induced by the bombardment of a particular nuclide of uranium or plutonium with neutrons.

When more than one neutron is released in each nuclide splitting, the fission reaction is a self-propagating reaction, or **chain reaction.** Neutrons released by one fission event may induce other fissions. When fission reactions are run under controlled conditions in a nuclear reactor, the energy released eventually appears as heat. The energy released by the fission of *one pound* of $^{235}_{92}U$ is equivalent to that obtained from more than *1000 tons* of coal.

Figure 21-6 shows that when very light nuclides such as $^{1}_{1}H$ or $^{2}_{1}H$ are brought together to form heavier elements, the binding energy per mole of nucleons again increases and energy is released. The graph also shows that the energy released per mole of nucleons is considerably greater in the fusion process than in the fission reaction. By use of a set of reactions in which four protons are converted into a helium nucleus and two electrons, *one pound* of hydrogen could produce energy equivalent to that obtained from *10,000 tons* of coal. For this reason, and because of the great abundance of hydrogen, fusion reactions are potentially sources of enormous amounts of energy. Unfortunately fusion reactions take place rapidly only at temperatures that are greater than a million degrees. These temperatures have been attained briefly by use of nuclear fission explosions. At present, attempts are being made to attain the temperatures required for nuclear fusion by less destructive means, so that these reactions can be used as an energy source. The most promising processes are based upon the fusion of deuterium, ${}^{2}_{1}H$, or tritium, ${}^{3}_{1}H$, nuclides. The immense amounts of energy generated in stars are a result of nuclear reactions. Different reactions are thought to occur at different stages in the lifetime of a star. The fusion of four protons to form one helium nucleus is responsible for the energy production during the longest period of a star's existence. The age of our star, the sun, is around 5×10^{9} years. It is estimated that there is enough hydrogen remaining in the sun to provide energy for 10×10^{9} more years.

21-6 Comparison of a Chemical and a Nuclear Reaction

Comparison of the H_2—I_2 iodine (${}^{127}I$) reaction with the proton—nuclear reaction will illustrate some similarities and emphasize some differences.

$$H_2 + I_2 \rightleftharpoons [H_2I_2] \rightleftharpoons HI + HI$$

(1) Collisions must involve sufficient energy to form the activated complex, H_2I_2. This minimum energy is called the activation energy.

(2) The activated complex decomposes very rapidly. The activated complex may form HI or it may form H_2 and I_2.

(3) For each mole of HI that forms from the gaseous elements about three kilocalories are released.

The nuclear reaction can be written

$${}^{1}_{1}H + {}^{127}_{53}I \leftrightarrows \left[{}^{128}_{54}Xe \right] \begin{array}{l} \nearrow {}^{124}_{52}Te + {}^{4}_{2}He \\ \rightarrow {}^{127}_{54}Xe + {}^{1}_{0}n \\ \searrow {}^{126}_{54}Xe + 2\,{}^{1}_{0}n \end{array}$$

(1) Collisions must involve sufficient energy to form the activated complex, ${}^{128}_{54}Xe$. The high-energy collisions occur when accelerated protons strike the sample of solid iodine.

(2) This intermediate is quite unstable and decomposes in about 10^{-14} to 10^{-18} second. The ${}^{128}_{54}Xe$ nuclide may return to ${}^{127}_{53}I$ plus a proton or form one pair of the products shown. Thus the inter-

mediate can change into the original reactants or new products, just as in a chemical reaction.

(3) For each mole of nuclear products, large amounts of energy may be released or absorbed. For the reaction that forms $^{127}_{54}Xe$, energies of the order of 50 million kcal/mole are absorbed. Even though this example is endothermic, it still serves to illustrate the huge energies observed for nuclear changes.

21-7 The Age of the Earth

One of the most interesting questions man has asked is, "How old is the earth?" We shall see that ingenious methods have been developed that enable scientists to determine the age of the earth's crust.

The most reliable methods for establishing the age of a long-lasting object (such as a mountain) depend upon the presence of natural radioactivity. For example, consider the chemical composition of a very old crystal of pitchblende, U_3O_8. We may presume that this crystal was formed at a time when chemical conditions for its formation were favorable. For example, it may have precipitated from molten rock during cooling. The resulting crystals tend to exclude impurities. Yet, careful analysis shows that every deposit of pitchblende contains a small amount of lead. Scientists assume the lead has come from uranium through radioactive decay.

The sequences of radioactive decays that eventually produce lead are well known, and the rates of decay have been carefully measured. We shall consider the sequence based upon the relatively slow decomposition of the most abundant uranium isotope, mass 238 (natural abundance, 99%):

$$^{238}_{92}U \longrightarrow {}^{4}_{2}He + {}^{234}_{90}Th \qquad \alpha\text{-decay, half-life, } T_{1/2} = 4.6 \times 10^9 \text{ years}$$

The products are an α-particle (a helium nucleus) and a thorium isotope that is unstable and that rapidly decays by emitting successively two electrons:

$$^{234}_{90}Th \longrightarrow {}^{234}_{91}Pa + {}^{0}_{-1}e \qquad \beta\text{-decay, } T_{1/2} = 24.1 \text{ days}$$
$$^{234}_{91}Pa \longrightarrow {}^{234}_{92}U + {}^{0}_{-1}e \qquad \beta\text{-decay, } T_{1/2} = 1.14 \text{ minutes}$$

Thus we have returned to an isotope of uranium, ^{234}U, but one of half-life very much shorter than that of ^{238}U. This isotope begins a succession of α-decays, each reducing the atomic number by two.

$$^{234}_{92}U \longrightarrow {}^{230}_{90}Th + {}^{4}_{2}He \qquad \alpha\text{-decay, } T_{1/2} = 2.7 \times 10^5 \text{ years}$$
$$^{230}_{90}Th \longrightarrow {}^{226}_{88}Ra + {}^{4}_{2}He \qquad \alpha\text{-decay, } T_{1/2} = 8.3 \times 10^4 \text{ years}$$
$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He \qquad \alpha\text{-decay, } T_{1/2} = 1.6 \times 10^3 \text{ years}$$
$$^{222}_{86}Rn \longrightarrow {}^{218}_{84}Po + {}^{4}_{2}He \qquad \alpha\text{-decay, } T_{1/2} = 3.8 \text{ days}$$
$$^{218}_{84}Po \longrightarrow {}^{214}_{82}Pb + {}^{4}_{2}He \qquad \alpha\text{-decay, } T_{1/2} = 3.1 \text{ minutes}$$

We have at last reached lead—but $^{214}_{82}Pb$ is itself radioactive! This isotope decays in a succession of β-decays:

${}^{214}_{82}\mathrm{Pb} \longrightarrow {}^{214}_{83}\mathrm{Bi} + {}^{0}_{-1}e$ β-decay, $T_{1/2} = 27$ minutes
${}^{214}_{83}\mathrm{Bi} \longrightarrow {}^{214}_{84}\mathrm{Po} + {}^{0}_{-1}e$ β-decay, $T_{1/2} = 20$ minutes

Again α-decay occurs, returning to the element lead, but to another isotope that decays by emitting successively two β-particles:

${}^{214}_{84}\mathrm{Po} \longrightarrow {}^{210}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He}$ α-decay, $T_{1/2} = 1.5 \times 10^{-4}$ second
${}^{210}_{82}\mathrm{Pb} \longrightarrow {}^{210}_{83}\mathrm{Bi} + {}^{0}_{-1}e$ β-decay, $T_{1/2} = 22$ years
${}^{210}_{83}\mathrm{Bi} \longrightarrow {}^{210}_{84}\mathrm{Po} + {}^{0}_{-1}e$ β-decay, $T_{1/2} = 5$ days

This isotope of polonium, ${}^{210}_{84}\mathrm{Po}$, again decays by α-decay, but *this time gives an isotope that does not decay further:*

${}^{210}_{84}\mathrm{Po} \longrightarrow {}^{206}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He}$ α-decay, $T_{1/2} = 140$ days
${}^{206}_{82}\mathrm{Pb} \longrightarrow$ not radioactive $T_{1/2}$ infinitely large

The final product in this long sequence of reactions is the stable isotope of lead, ${}^{206}\mathrm{Pb}$. *The amount of ${}^{206}Pb$ present depends upon how long the deposit of uranium has been decaying since it was formed.*

There is, fortunately, a rather simple verification of the presumption that all of the lead came from this long sequence of nuclear reactions. Lead ores that do not contain uranium include several isotopes—${}^{206}\mathrm{Pb}$ makes up about 26% of the total and the rest is ${}^{204}\mathrm{Pb}$ (1.4%), ${}^{207}\mathrm{Pb}$ (21%), and ${}^{208}\mathrm{Pb}$ (52%). Of these, two are formed through radioactive decay of some other uranium or thorium isotope by a sequence like that shown for ${}^{238}\mathrm{U}$. Of the four stable lead isotopes, the only one *not* derived from known radioactive decay series is ${}^{204}\mathrm{Pb}$. Hence, the ratio of the amount of this isotope to that of ${}^{206}\mathrm{Pb}$ measures the amount of ${}^{206}\mathrm{Pb}$ present in excess of the natural abundance. This excess comes from decay of ${}^{238}\mathrm{U}$. If there is *no* ${}^{204}\mathrm{Pb}$ present, then all of the ${}^{206}\mathrm{Pb}$ came from ${}^{238}\mathrm{U}$.

Thus, analysis of uranium minerals with the aid of the mass spectrograph gives information on the age of the mineral. Though many different half-lives are involved in forming the lead, only the longest half-life (the rate-determining step) is of importance. *Combining the lead content with the ${}^{238}U$ half-life provides estimates of mineral ages in the range of five billion years.*

What have we learned in this estimate? Surely we can say the age of the earth cannot be *less* than 5×10^{9} years. To evaluate this number further, we must look for other types of data.

Fortunately, there are other radioactive elements in nature that give similar bases for estimates. As a second example, potassium in nature includes one radioactive isotope, ${}^{40}_{19}\mathrm{K}$, which decays by capturing an electron into its nucleus. The product is ${}^{40}_{18}\mathrm{Ar}$, a stable isotope:

${}^{40}_{19}\mathrm{K} + {}^{0}_{-1}e \longrightarrow {}^{40}_{18}\mathrm{Ar}$ electron capture $T_{1/2} = 1.5 \times 10^{10}$ years

Once again, the ratio of the abundance in a crystal of the two isotopes, $^{40}Ar/^{40}K$, provides a clue to the age of the crystal. Mica is a mineral that has been much studied in this type of mineral age estimation. Such estimates also tend to date the minerals as a few billion years old. Similar age figures are obtained from the natural radioactivity of rubidium.

In conclusion, the agreement of all of these methods based upon radioactive decay furnishes a strong clue that the earth's crust *as we know it today* was formed about five billion years ago.

21-8 Radiocarbon Dating

In the atmosphere, bombardment by neutrons from cosmic rays produces $^{14}_{6}C$ by the reaction

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

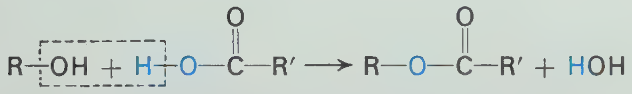
The carbon nuclide has a half-life of 5570 years and decays in accord with

$$^{14}_{6}C \longrightarrow {}^{0}_{-1}e + ^{14}_{7}N$$

The concentration of $^{14}CO_2$ in the atmosphere is kept constant at 1 radioatom per 10^{12} stable carbon atoms by a steady-state balance of production, decay. Living plants and animals establish a balance with the atmospheric $^{14}CO_2$ so that they reach a stationary level of ^{14}C content. Upon death this balance is upset and the ^{14}C begins to decay without being replaced. Measurement of the ^{14}C radioactivity in a specimen permits calculation of how long ago death took place. By such means it has been shown that the Dead Sea Scrolls are about two thousand years old with a precision of ±200 years.

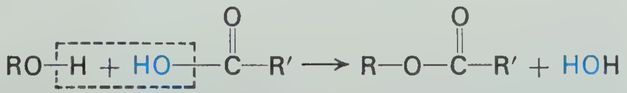
21-9 Isotopic Tagging

Sometimes radioactive isotopes of convenient half-lives are not available. In these cases stable isotopes are used and their presence detected by a mass spectrometer. Let us consider the reaction of esterification between an organic alcohol and an organic acid. The splitting of water between the alcohol and acid can occur in two ways. One method is by the mechanism



$$R{-}OH + H{-}O{-}\overset{\overset{O}{\|}}{C}{-}R' \longrightarrow R{-}O{-}\overset{\overset{O}{\|}}{C}{-}R' + HOH$$

in which the oxygen of the alcohol goes into the water molecule. The second possibility is by means of



$$RO{-}H + HO{-}\overset{\overset{O}{\|}}{C}{-}R' \longrightarrow R{-}O{-}\overset{\overset{O}{\|}}{C}{-}R' + HOH$$

in which the alcohol oxygen finds a place in the ester molecule.

In one common example, methyl alcohol is tagged by using ^{18}O in its synthesis so that $CH_3{}^{18}OH$ is formed. When this alcohol is reacted with benzoic acid, the mass spectrometer shows that the ^{18}O nuclide is in the ester and not in the water. This pair of chemicals reacts according to the second mechanism.

Questions and Problems for Chapter 21

1

Describe the spectrum produced on a photographic plate in a mass spectrograph if a mixture of the isotopes of oxygen (^{16}O, ^{17}O, and ^{18}O) is analyzed. Consider only the record for 1+ and 2+ ions.

2

Hydroxylamine, NH_2OH, is subjected to electron bombardment. The products are passed through a mass spectrograph. The two pairs of lines formed indicate charge/mass ratios of 0.0625, 0.0588 and 0.1250, 0.1176. How can this be interpreted?

3

In a nuclear reaction of the type called "nuclear fusion," two nuclei come together to form a larger nucleus. For example, deuterium nuclei, ^2_1H, and tritium nuclei, ^3_1H, can "fuse" to form helium nuclei, ^4_2He, and a neutron:

$$^2_1H + ^3_1H \longrightarrow ^4_2He + ^1_0n \qquad \Delta H = -4.05 \times 10^7 \text{ kcal}$$

How many grams of hydrogen would have to be burned (to gaseous water) to liberate the same amount of heat as liberated by fusion of one mole of ^2_1H nuclei? Express the answer in tons (1 ton = 9.07×10^5 g).

4

Write equations for the following reactions:

(a) beta decay of $^{253}_{98}Cf$.
(b) alpha decay of $^{253}_{100}Fm$.
(c) the formation of $^{120}_{50}Sn$ by positron emission from an antimony isotope.

5

The half-life of $^{253}_{100}Fm$ is 4.5 days. What fraction of a mole of fermium would remain after 13.5 days (three half-lives)?

6

The half-life of $^{125}_{53}I$ is 60 days. What percent of original radioactivity would be present after 360 days?

7

The $^{14}_6C$ nuclide undergoes beta decay.

(a) What stable nuclide is formed?
(b) Demonstrate the electron balance in the equation.
(c) The mass difference between reactants and products is 1.66×10^{-4} g/mole. Calculate the total energy in kcal released in this process.

8

Fission of uranium gives a variety of fission products, including praseodymium, Pr. If the process by which praseodymium is formed gives $^{147}_{59}Pr$ and three neutrons, what is the other nuclear product?

$$^{235}_{92}U + ^1_0n \longrightarrow ^{147}_{59}Pr + ? + 3\,^1_0n$$

9

For $^{16}_8O$, the mass difference between products and reactants in the equation

$$8\,^1_1H + 8\,^1_0n \longrightarrow ^{16}_8O$$

is 0.137 g/mole. Calculate the binding energy per nucleon in $^{16}_8O$ as kcal per mole.

10

Which of the following reactions is most likely to have a heat effect of −505 kcal? Which would be -1.7×10^6 kcal? Which would be +7.2 kcal?

(a) $UF_6(l) \longrightarrow UF_6(g) \qquad \Delta H = ?$
(b) $U(s) + 3\,F_2(g) \longrightarrow UF_6(l) \qquad \Delta H = ?$
(c) $^{238}_{92}U + ^1_0n \longrightarrow ^{239}_{92}U \qquad \Delta H = ?$

11

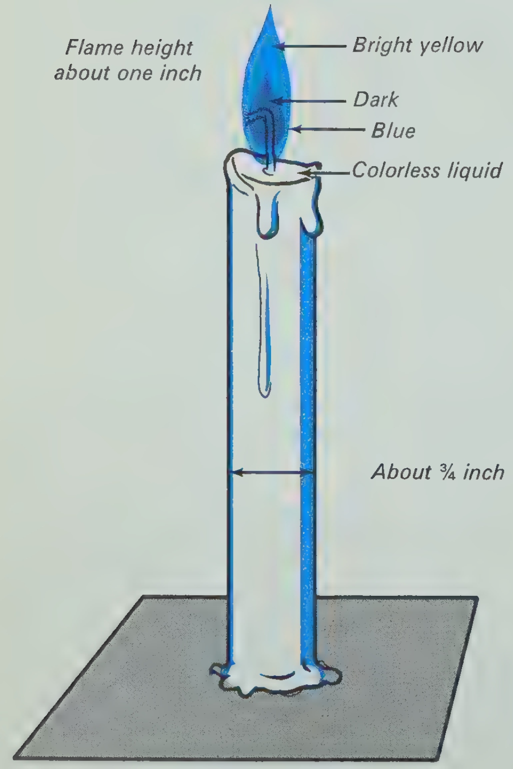
A piece of wood recently obtained from a living plant will give carbon having 15.2 ± 0.1 beta particles/min/gram. What age is a sample that gives 3.8 beta particles/min/gram?

Appendices

Appendix 1. A Description of a Burning Candle
Appendix 2. Names, Formulas, and Charges of Some Common Ions
Appendix 3. Relative Strengths of Acids in Aqueous Solution
Appendix 4. Standard Oxidation Potentials for Half-Reactions

Appendix 1

A DESCRIPTION OF A BURNING CANDLE



A drawing of a burning candle is shown[1] in the figure to the left. The candle is cylindrical in shape[2] and has a diameter[3] of about $\frac{3}{4}$ inch. The length of the candle was initially about eight inches[4] and it changed slowly[5] during observation, decreasing about half an inch in one hour[6]. The candle is made of a translucent[7], white[8] solid[9] which has a slight odor[10] and no taste[11]. It is soft enough to be scratched with the fingernail[12]. There is a wick[13] which extends from top to bottom[14] of the candle along its central axis[15] and protrudes about half an inch above the top of the candle[16]. The wick is made of three strands of string braided together[17].

A candle is lit by holding a source of flame close to the wick for a few seconds. Thereafter the source of flame can be removed and the flame sustains itself at the wick[18]. The burning candle makes no sound[19]. While burning, the body of the candle remains cool to the touch[20] except near the top. Within about half an inch from the top the candle is warm[21] (but not hot) and sufficiently soft to mold easily[22]. The flame flickers in response to air currents[23] and tends to become quite smoky while flickering[24]. In the absence of air currents, the flame is of the form shown in the figure, though it retains some movement at all times[25]. The flame begins about $\frac{1}{8}$ inch above the top of the candle[26] and at its base the flame has a blue tint[27]. Immediately around the wick in a region about $\frac{1}{4}$ inch wide and extending about $\frac{1}{2}$ inch above the top of the wick[28] the flame is dark[29]. This dark region is roughly conical in shape[30]. Around this zone and extending about half an inch above the dark zone is a region which emits yellow light[31], bright but not blinding[32]. The flame has rather sharply defined sides[33], but a ragged top[34]. The wick is white where it emerges from the candle[35], but from the base of the flame to the end of the wick[36] it is black, appearing burnt, except for the last $\frac{1}{16}$ inch where it glows red[37]. The wick curls over about $\frac{1}{4}$ inch from its end[38]. As the candle becomes shorter, the wick shortens too, so as to extend roughly a constant length above the top of the candle[39]. Heat is emitted by the flame[40], enough so that it becomes uncomfortable in ten or twenty seconds if one holds his finger $\frac{1}{4}$ inch to the side of the quiet flame[41] or three or four inches above the flame[42].

The top of a quietly burning candle becomes wet with a colorless liquid[43] and becomes bowl shaped[44]. If the flame is blown, one side of this bowl-shaped top may become liquid, and the liquid trapped in the bowl may drain down the candle's side[45]. As it courses down, the colorless liquid cools[46], becomes translucent[47], and gradually solidifies from the outside[48], attaching itself to the side of the candle[49]. In the absence of a draft, the candle can burn for hours without such dripping[50]. Under these conditions, a stable pool of clear liquid remains in the bowl-shaped top of the candle[51]. The liquid rises slightly around the wick[52], wetting the base of the wick as high as the base of the flame[53].

COMMENTS

Several aspects of this description deserve specific mention. Compare your own description in each of the following characteristics.

1. The description is comprehensive in *qualitative* terms. Did *you* include mention of appearance? smell? taste? feel? sound? (Note: A chemist quickly becomes reluctant to taste or smell an unknown chemical. A chemical should be considered to be poisonous unless it is *known* not to be!)
2. Wherever possible, the description is stated *quantitatively.* This means the question "How much?" is answered (the quantity is specified). The remark that the flame emits yellow light is made more meaningful by the "how much" expression, "bright but not blinding." The statement that heat is emitted might lead a cautious investigator who is lighting a candle for the first time to stand in a concrete blockhouse one hundred yards away. The few words telling him "how much" heat would save him this overprecaution.
3. The description does not presume the importance of an observation. Thus the observation that a burning candle does not emit sound deserves to be mentioned just as much as the observation that it does emit light.
4. The description does not confuse observations with interpretations. It is an observation that the top of the burning candle is wet with a colorless liquid. It would be an interpretation to state the presumed composition of this liquid.

Appendix 2

NAMES, FORMULAS, AND CHARGES OF SOME COMMON IONS

POSITIVE IONS (CATIONS)		NEGATIVE IONS (ANIONS)	
aluminum	Al^{3+}	acetate	CH_3COO^-
ammonium	NH_4^+	bromide	Br^-
barium	Ba^{2+}	carbonate	CO_3^{2-}
calcium	Ca^{2+}	hydrogen carbonate ion, bicarbonate	HCO_3^-
chromium(II), chromous	Cr^{2+}	chlorate	ClO_3^-
chromium(III), chromic	Cr^{3+}	chloride	Cl^-
copper(I),* cuprous	Cu^+	chlorite	ClO_2^-
copper(II), cupric	Cu^{2+}	chromate	CrO_4^{2-}
hydrogen, hydronium	H^+, H_3O^+	dichromate	$Cr_2O_7^{2-}$
iron(II),* ferrous	Fe^{2+}	fluoride	F^-
iron(III), ferric	Fe^{3+}	hydroxide	OH^-
lead	Pb^{2+}	hypochlorite	ClO^-
lithium	Li^+	iodide	I^-
magnesium	Mg^{2+}	nitrate	NO_3^-
manganese(II), manganous	Mn^{2+}	nitrite	NO_2^-
mercury(I),* mercurous	Hg_2^{2+}	oxalate	$C_2O_4^{2-}$
mercury(II), mercuric	Hg^{2+}	hydrogen oxalate ion, binoxalate	$HC_2O_4^-$
potassium	K^+	perchlorate	ClO_4^-
silver	Ag^+	permanganate	MnO_4^-
sodium	Na^+	phosphate	PO_4^{3-}
tin(II),* stannous	Sn^{2+}	monohydrogen phosphate	HPO_4^{2-}
tin(IV), stannic	Sn^{4+}	dihydrogen phosphate	$H_2PO_4^-$
zinc	Zn^{2+}	sulfate	SO_4^{2-}
		hydrogen sulfate ion, bisulfate	HSO_4^-
		sulfide	S^{2-}
		hydrogen sulfide ion, bisulfide	HS^-
		sulfite	SO_3^{2-}
		hydrogen sulfite ion, bisulfite	HSO_3^-

* Aqueous solutions are readily oxidized by air.

Note: In ionic compounds the relative number of positive and negative ions is such that the sum of their electric charges is zero.

Appendix 3

RELATIVE STRENGTHS OF ACIDS IN AQUEOUS SOLUTION AT ROOM TEMPERATURE

All ions are aquated

$$HB \rightleftharpoons H^+(aq) + B^-(aq) \qquad K_A = \frac{[H^+][B^-]}{[HB]}$$

ACID	STRENGTH	REACTION	K_A
perchloric acid	very strong	$HClO_4 \longrightarrow H^+ + ClO_4^-$	very large
hydroiodic acid		$HI \longrightarrow H^+ + I^-$	very large
hydrobromic acid		$HBr \longrightarrow H^+ + Br^-$	very large
hydrochloric acid		$HCl \longrightarrow H^+ + Cl^-$	very large
nitric acid		$HNO_3 \longrightarrow H^+ + NO_3^-$	very large
sulfuric acid	very strong	$H_2SO_4 \longrightarrow H^+ + HSO_4^-$	large
hydrated hydrogen ion		$H_3O^+ \longrightarrow H^+ + H_2O$	1.00
oxalic acid		$HOOCCOOH \longrightarrow H^+ + HOOCCOO^-$	5.4×10^{-2}
sulfurous acid ($SO_2 + H_2O$)		$H_2SO_3 \longrightarrow H^+ + HSO_3^-$	1.7×10^{-2}
hydrogen sulfate ion	strong	$HSO_4^- \longrightarrow H^+ + SO_4^{2-}$	1.3×10^{-2}
phosphoric acid		$H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$	7.1×10^{-3}
ferric ion		$Fe(H_2O)_6^{3+} \longrightarrow H^+ + Fe(H_2O)_5(OH)^{2+}$	6×10^{-3}
hydrogen telluride		$H_2Te \longrightarrow H^+ + HTe^-$	2.3×10^{-3}
hydrofluoric acid	weak	$HF \longrightarrow H^+ + F^-$	6.7×10^{-4}
nitrous acid		$HNO_2 \longrightarrow H^+ + NO_2^-$	5.1×10^{-4}
hydrogen selenide		$H_2Se \longrightarrow H^+ + HSe^-$	1.7×10^{-4}
chromic ion		$Cr(H_2O)_6^{3+} \longrightarrow H^+ + Cr(H_2O)_5(OH)^{2+}$	10^{-4}
benzoic acid		$C_6H_5COOH \longrightarrow H^+ + C_6H_5COO^-$	6.6×10^{-5}
hydrogen oxalate ion		$HOOCCOO^- \longrightarrow H^+ + OOCCOO^{2-}$	5.4×10^{-5}
acetic acid	weak	$CH_3COOH \longrightarrow H^+ + CH_3COO^-$	1.8×10^{-5}
aluminum ion		$Al(H_2O)_6^{3+} \longrightarrow H^+ + Al(H_2O)_5(OH)^{2+}$	10^{-5}
hydrogen telluride ion		$HTe^- \longrightarrow H^+ + Te^{2-}$	10^{-5}
carbonic acid ($CO_2 + H_2O$)		$H_2CO_3 \longrightarrow H^+ + HCO_3^-$	4.4×10^{-7}
hydrogen sulfide		$H_2S \longrightarrow H^+ + HS^-$	1.0×10^{-7}
dihydrogen phosphate ion		$H_2PO_4^- \longrightarrow H^+ + HPO_4^{2-}$	6.3×10^{-8}
hydrogen sulfite ion	weak	$HSO_3^- \longrightarrow H^+ + SO_3^{2-}$	6.2×10^{-8}
ammonium ion		$NH_4^+ \longrightarrow H^+ + NH_3$	5.7×10^{-10}
hydrogen carbonate ion		$HCO_3^- \longrightarrow H^+ + CO_3^{2-}$	4.7×10^{-11}
hydrogen peroxide	very weak	$H_2O_2 \longrightarrow H^+ + HO_2^-$	2.4×10^{-12}
monohydrogen phosphate ion		$HPO_4^{2-} \longrightarrow H^+ + PO_4^{3-}$	4.4×10^{-13}
hydrogen sulfide ion		$HS^- \longrightarrow H^+ + S^{2-}$	1.3×10^{-13}
water		$H_2O \longrightarrow H^+ + OH^-$	1.0×10^{-14}
hydroxide ion		$OH^- \longrightarrow H^+ + O^{2-}$	$< 10^{-36}$
ammonia	very weak	$NH_3 \longrightarrow H^+ + NH_2^-$	very small

Appendix 4

STANDARD OXIDATION POTENTIALS FOR HALF-REACTIONS IONIC CONCENTRATIONS, 1 *M* IN WATER AT 25°

All ions are aquated

	HALF-REACTION	$E°$ (volts)	
Very strong reducing agents	$Li \longrightarrow e^- + Li^+$	3.00	Very weak oxidizing agents
	$Rb \longrightarrow e^- + Rb^+$	2.92	
	$K \longrightarrow e^- + K^+$	2.92	
	$Cs \longrightarrow e^- + Cs^+$	2.92	
	$Ba \longrightarrow 2\,e^- + Ba^{2+}$	2.90	
	$Sr \longrightarrow 2\,e^- + Sr^{2+}$	2.89	
	$Ca \longrightarrow 2\,e^- + Ca^{2+}$	2.87	
	$Na \longrightarrow e^- + Na^+$	2.71	
	$Mg \longrightarrow 2\,e^- + Mg^{2+}$	2.37	
	$Al \longrightarrow 3\,e^- + Al^{3+}$	1.66	
	$Mn \longrightarrow 2\,e^- + Mn^{2+}$	1.18	
	$H_2(g) + 2\,OH^- \longrightarrow 2\,e^- + 2\,H_2O$	0.83	
	$Zn \longrightarrow 2\,e^- + Zn^{2+}$	0.76	
Reducing strength increases	$Cr \longrightarrow 3\,e^- + Cr^{3+}$	0.74	Oxidizing strength increases
	$H_2Te \longrightarrow 2\,e^- + \frac{1}{8}\,Te_8 + 2\,H^+$	0.72	
	$2\,Ag + S^{2-} \longrightarrow 2\,e^- + Ag_2S$	0.69	
	$Fe \longrightarrow 2\,e^- + Fe^{2+}$	0.44	
	$H_2(g) \longrightarrow 2\,e^- + 2\,H^+\ (10^{-7}\,M)$	0.414	
	$Cr^{2+} \longrightarrow e^- + Cr^{3+}$	0.41	
	$H_2Se \longrightarrow 2\,e^- + \frac{1}{8}\,Se_8 + 2\,H^+$	0.40	
	$Pb + SO_4^{2-} \longrightarrow 2\,e^- + PbSO_4$	0.36	
	$Co \longrightarrow 2\,e^- + Co^{2+}$	0.28	
	$Ni \longrightarrow 2\,e^- + Ni^{2+}$	0.25	
	$Sn \longrightarrow 2\,e^- + Sn^{2+}$	0.14	
	$Pb \longrightarrow 2\,e^- + Pb^{2+}$	0.13	
	$H_2(g) \longrightarrow 2\,e^- + 2\,H^+$	0.00	
	$H_2S(g) \longrightarrow 2\,e^- + \frac{1}{8}\,S_8 + 2\,H^+$	−0.14	
	$Sn^{2+} \longrightarrow 2\,e^- + Sn^{4+}$	−0.15	
	$Cu^+ \longrightarrow e^- + Cu^{2+}$	−0.15	
	$SO_2(g) + 2\,H_2O \longrightarrow 2\,e^- + SO_4^{2-} + 4\,H^+$	−0.17	
	$Cu \longrightarrow 2\,e^- + Cu^{2+}$	−0.34	
	$Cu \longrightarrow e^- + Cu^+$	−0.52	
	$2\,I^- \longrightarrow 2\,e^- + I_2$	−0.53	
	$H_2O_2 \longrightarrow 2\,e^- + O_2(g) + 2\,H^+$	−0.68	

	HALF-REACTION	E° (volts)	
Reducing strength increases	$Fe^{2+} \longrightarrow e^- + Fe^{3+}$	-0.77	Oxidizing strength increases
	$NO_2(g) + H_2O \longrightarrow e^- + NO_3^- + 2\,H^+$	-0.78	
	$Hg(l) \longrightarrow 2\,e^- + Hg^{2+}$	-0.78	
	$Hg(l) \longrightarrow e^- + \frac{1}{2}\,Hg_2^{2+}$	-0.79	
	$Ag \longrightarrow e^- + Ag^+$	-0.80	
	$H_2O \longrightarrow 2\,e^- + \frac{1}{2}\,O_2(g) + 2\,H^+\ (10^{-7}\,M)$	-0.815	
	$NO(g) + 2\,H_2O \longrightarrow 3\,e^- + NO_3^- + 4\,H^+$	-0.96	
	$Au + 4\,Cl^- \longrightarrow 3\,e^- + AuCl_4^-$	-1.00	
	$2\,Br^- \longrightarrow 2\,e^- + Br_2(l)$	-1.06	
	$H_2O \longrightarrow 2\,e^- + \frac{1}{2}\,O_2(g) + 2\,H^+$	-1.23	
	$Mn^{2+} + 2\,H_2O \longrightarrow 2\,e^- + MnO_2 + 4\,H^+$	-1.28	
	$2\,Cr^{3+} + 7\,H_2O \longrightarrow 6\,e^- + Cr_2O_7^{2-} + 14\,H^+$	-1.33	
	$2\,Cl^- \longrightarrow 2\,e^- + Cl_2(g)$	-1.36	
	$Au \longrightarrow 3\,e^- + Au^{3+}$	-1.50	
	$Mn^{2+} + 4\,H_2O \longrightarrow 5\,e^- + MnO_4^- + 8\,H^+$	-1.52	
Very weak reducing agents	$PbSO_4 + 2\,H_2O \longrightarrow 2\,e^- + H^+ + SO_4^{2-} + PbO_2$	-1.68	Very strong oxidizing agents
	$2\,H_2O \longrightarrow 2\,e^- + H_2O_2 + 2\,H^+$	-1.77	
	$2\,F^- \longrightarrow 2\,e^- + F_2(g)$	-2.87	

Symbols and Abbreviations

Page numbers refer to the first reference. See inside back cover for symbols for elements.

A	mass number, 135
Å	Ångstrom, 10^{-8} cm, 143
(aq)	indicates an ion is aquated, 92
atm	atmosphere (pressure unit), 7
c	velocity of light, 137
°C	Celsius degree, 7
e	charge on electron, 129
e^-	electron, 91
E	energy, 125
$E°$	electrical potential, 289
g	gram, 16
(g)	indicates gas phase, 76
h	Planck's constant,
H	heat content, 195
IE	ionization energy, 160
°K	Kelvin, or absolute degree, 57
K	equilibrium constant, 240
K_A	equilibrium constant for acid ionization, 266
K_{sp}	solubility product, 242
K_w	$[H^+][OH^-]$, ion product of water, 241
kcal	kilocalorie, 43
KE	kinetic energy, 60
(l)	indicates liquid phase, 74
m	mass of the electron, 129
M	molarity, moles/liter, 86
ml	milliliter, 13
mm	millimeter, 7
n	neutron, 135
n	principal quantum number, 145
N	Avogadro's number, particles/mole, 6.0×10^{23}, 32
N	number of neutrons in a nucleus, 137
Ox. no.	Oxidation number, 306
p	type of orbital, 148
p or p^+	proton, 91
P	pressure, 12
R	general alkyl group, 358
s	type of orbital, 147
(s)	indicates solid phase, 76
STP	standard temperature and pressure (0°C and 1 atm), 7
t	temperature, C, 10
T	temperature, °K, 57
$T_{1/2}$	half-life, 417
V	volume, 12
Z	atomic number, number of protons in nucleus, 137
Δ (delta)	change, 14
λ (lambda)	wavelength, 123
ν (nu)	frequency, 123
α (alpha)	particles, He^{2+}, 132
β or β^- (beta)	particles, e^-, 132
γ (gamma)	radiation, 132
○	empty orbital, 151
⊘ ⦸	half-filled orbitals, 151
⊗	filled orbital, 151

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INTERNATIONAL MOLAR MASSES

NAME	SYMBOL	ATOMIC NUMBER	MOLAR MASS
Actinium	Ac	89	(227)
Aluminum	Al	13	27.0
Americium	Am	95	(243)
Antimony	Sb	51	121.8
Argon	Ar	18	39.9
Arsenic	As	33	74.9
Astatine	At	85	(210)
Barium	Ba	56	137.3
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	209.0
Boron	B	5	10.8
Bromine	Br	35	79.9
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.1
Californium	Cf	98	(251)
Carbon	C	6	12.01
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.5
Chromium	Cr	24	52.0
Cobalt	Co	27	58.9
Copper	Cu	29	63.5
Curium	Cm	96	(248)
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	(254)
Erbium	Er	68	167.3
Europium	Eu	63	152.0
Fermium	Fm	100	(253)
Fluorine	F	9	19.0
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.2
Gallium	Ga	31	69.7
Germanium	Ge	32	72.6
Gold	Au	79	197.0
Hafnium	Hf	72	178.5
Helium	He	2	4.00
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.8
Krypton	Kr	36	83.8
Lanthanum	La	57	138.9
Lawrencium	Lw	103	(259)
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Lutetium	Lu	71	175.0
Magnesium	Mg	12	24.3
Manganese	Mn	25	54.9
Mendelevium	Md	101	(256)
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.9
Neodymium	Nd	60	144.2
Neon	Ne	10	20.2
Neptunium	Np	93	(237)
Nickel	Ni	28	58.7
Niobium	Nb	41	92.9
Nitrogen	N	7	14.01
Nobelium	No	102	(253)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	31.0
Platinum	Pt	78	195.1
Plutonium	Pu	94	(242)
Polonium	Po	84	210
Potassium	K	19	39.1
Praseodymium	Pr	59	140.9
Promethium	Pm	61	(145)
Protactinium	Pa	91	(231)
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.5
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.4
Scandium	Sc	21	45.0
Selenium	Se	34	79.0
Silicon	Si	14	28.1
Silver	Ag	47	107.9
Sodium	Na	11	23.0
Strontium	Sr	38	87.6
Sulfur	S	16	32.1
Tantalum	Ta	73	180.9
Technetium	Tc	43	(99)
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.0
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.9
Tungsten	W	74	183.9
Uranium	U	92	238.0
Vanadium	V	23	50.9
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.9
Zinc	Zn	30	65.4
Zirconium	Zr	40	91.2
(unnamed)*	?	104	(260)

* Discovery reported in 1964.

Molar masses based on ^{12}C + 12.000.

Numbers in parentheses give the mass number of the most stable isotope.

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